CHEMICAL REVIEWS

REVIEW

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Fluorescent Dyes and Their Supramolecular Host/Guest Complexes with Macrocycles in Aqueous Solution

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CONTENTS

1. INTRODUCTION

The fluorescence of organic molecules depends sensitively on their environment. Fluorescent dyes have accordingly become popular molecular probes not only to determine microenvironmental parameters, such as the polarity of media, but also to follow their relocation and distribution dynamics in microheterogeneous systems such as membranes, micelles, and cellular media as well as interfaces, polymers, and discrete supramolecular systems. They have been found particularly useful to monitor the formation of discrete host/guest complexes with macrocyclic structures, which can serve as molecular containers (nanocavities) of fluorescent dyes. The inclusion of the dye into their (generally hydrophobic) cavity is accompanied by a large change in the microenvironmental parameters, which has been abundantly used in supramolecular chemistry to determine, on one hand, the association thermodynamics and kinetics and, on the other hand, the binding of competitors by indicator displacement methodologies. In fact, the binding of fluorescent dyes provides a *par excellence* educational example for the formation of supramolecular assemblies, which dates back to the first observation of room temperature luminescence in cyclodextrins[1,2] and has later found additional use for other, mostly polarity-sensitive, dyes.[3−5]

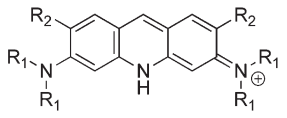
The interactions of macrocyclic hosts with fluorescent dyes have been summarized for subclasses and application examples,[6−8] but they have not been comprehensively reviewed. The present review focuses on water-soluble organic macrocycles and fluorescent guests with the perspective of using them for potential biological and environmental applications in the areas of sensing and signaling; the survey is consequently limited to the common dye classes, and other examples are only included if they produce noteworthy photophysical effects upon macrocyclic encapsulation. Covalently preorganized macrocycle−dye conjugates[9−14] have been in part reviewed elsewhere and will not be covered. Similarly, more specialized bis-macrocyclic systems have been previously reviewed.[15,16] Furthermore, transition metal-based chemosensing ensembles including macrocycles as scaffolds are also excluded.[17−20] For general background information, the reader is referred to textbooks in the areas of supramolecular chemistry,[21−26] supramolecular photochemistry,[27,28] fluorescent dyes,[29,30] and their use for the determination of binding constants of host/guest complexes.[31−33]

We will review which fluorescent dyes have been most extensively employed in aqueous solution and with which

Received: June 10, 2011
Published: October 07, 2011

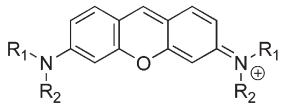
Scheme 1. Acridine and Xanthene Dyes

acridine dyes

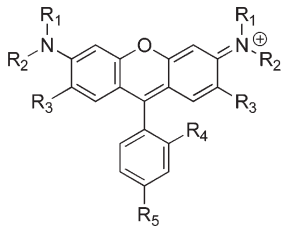


R_1	R_2	
H	H	proflavin (**PF**)
CH_4	H	acridine orange (**AO**)
H	CH_3	acridine yellow (**AY**)

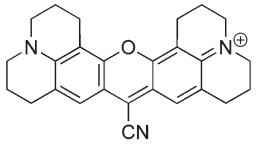
xanthene dyes (fluorenes)



R_1	R_2	
CH_3	H	acridine red (**AR**)
H	H	pyronine (**PY**)
CH_3	CH_3	pyronine Y (**PYY**)
C_2H_5	C_2H_5	pyronine B (**PYB**)

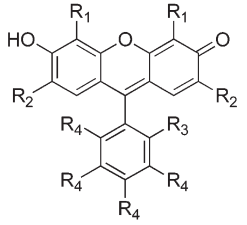


R_1	R_2	R_3	R_4	R_5	
C_2H_5	C_2H_5	H	COOH	H	rhodamine B (**RhB**)
C_2H_5	C_2H_5	H	$COOC_4H_9$	H	butyl rhodamine B (**BRB**)
H	C_2H_5	CH_3	$COOC_2H_5$	H	rhodamine 6G (**R6G**)
H	H	H	$COOC_2H_5$	H	rhodamine 123 (**R123**)
CH_3	CH_3	H	COOH	H	tetramethylrhodamine (**TMR**)
C_2H_5	C_2H_5	H	SO_3H	SO_3H	kiton red S (**KRS**)
C_2H_5	C_2H_5	H	COOBn	H	rhodamine B benzyl ester (**RhBBE**)



rhodamine 800 (**Rh800**)

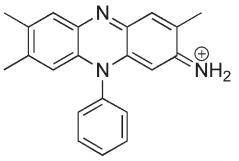
xanthene dyes (fluorones)



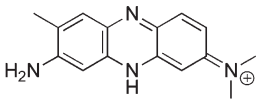
R_1	R_2	R_3	R_4	
I	I	COONa	H	erythrosine sodium (**ES**)
H	H	COONa	H	fluorescein sodium (**FS**)
H	OH	OH	H	salicyl fluorone (**SAF**)
I	I	COONa	Cl	tetrachlorotetraiodofluorescein (**TCTIF**)
H	H	COONa	Cl	tetrachlorofluorescein (**TCF**)

Scheme 2. Quinone-imine, Arylmethane, and Azo Dyes

quinone-imine dyes (azines)

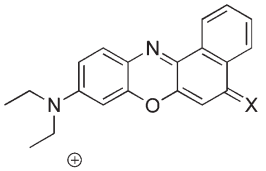


safranine T (**ST**)

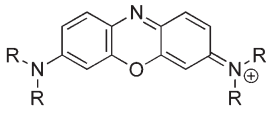


neutral red (**NR**)

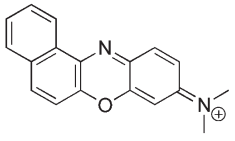
quinone-imine dyes (oxazines)



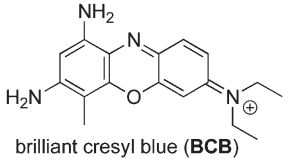
X = NH_2 nile blue (**NiB**)
X = O nile red (**NiR**)



R = H oxonine (**OX**)
R = C_2H_5 oxazine 1 (**OX1**) or oxazine 725

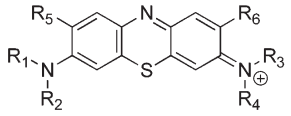


Meldola's blue (**MDB**)



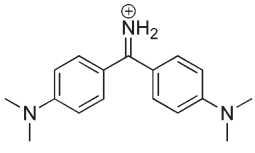
brilliant cresyl blue (**BCB**)

quinone-imine dyes (thiazines)

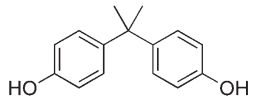


R_1	R_2	R_3	R_4	R_5	R_6	
H	H	H	H	H	H	thionine (**TH**)
H	H	CH_3	CH_3	H	H	azure A (**AZA**)
CH_3	CH_3	CH_3	CH_3	H	H	methylene blue (**MB**)
H	H	CH_3	CH_3	CH_3	H	toluidine blue (**TB**)
H	C_2H_5	H	C_2H_5	CH_3	CH_3	new methylene blue (**NMB**)

arylmethane dyes



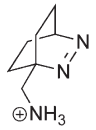
auramine O (**AuO**)



bisphenol A (**BPA**)

azo dyes

DBO

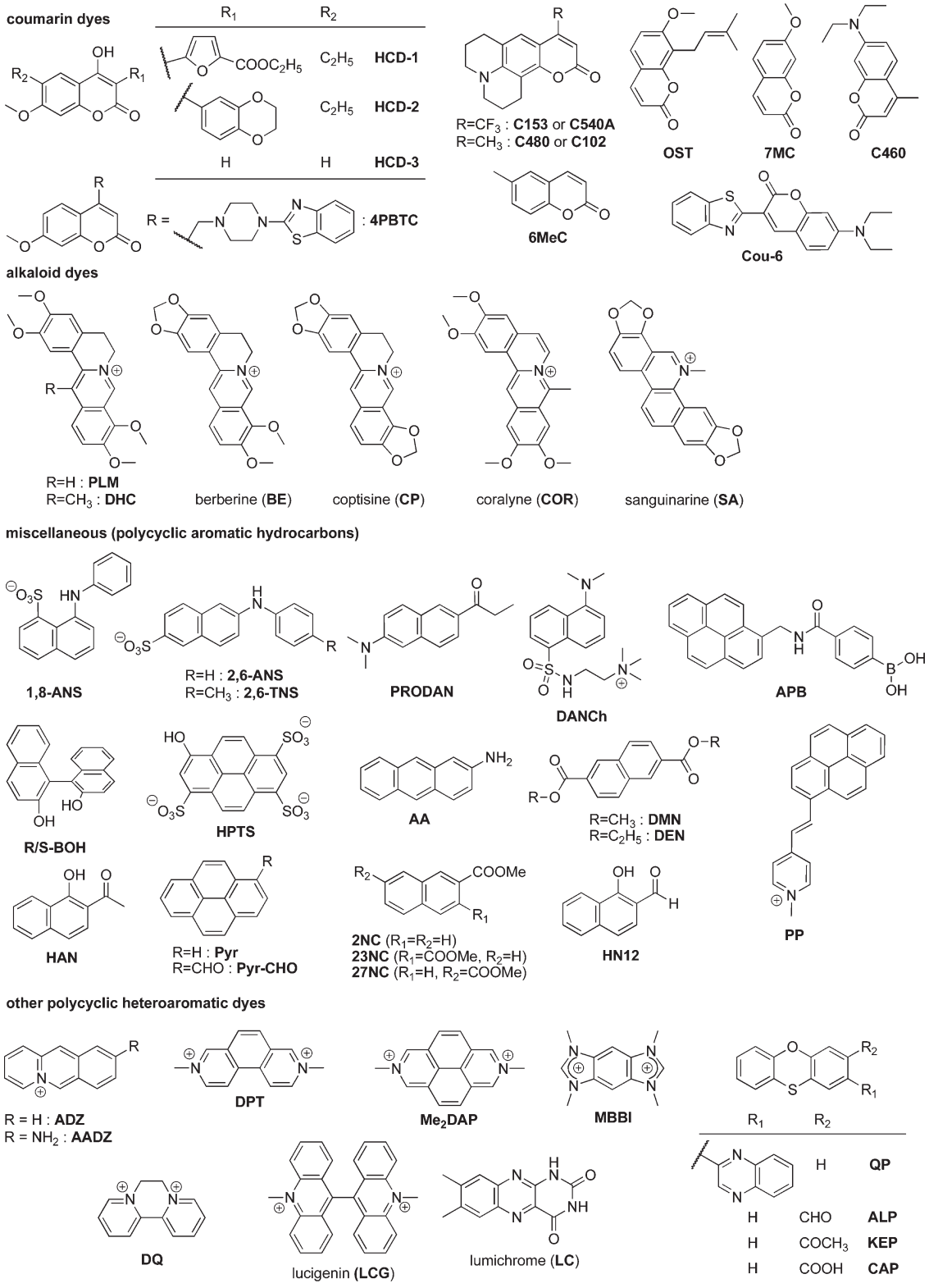


DBO-Amine

water-soluble macrocyclic hosts they have been used in combination, how they have been utilized as solvatochromic probes to obtain information about the hydrophobicity, polarity, and polarizability of the inner supramolecular concave phases, how their UV−vis absorption and emission properties are affected, and how their complex formation can be applied for sensing, imaging, lasing, stabilizing, and other purposes. An emphasis will be given to examples in which binding constants, spectral shifts,

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Scheme 3. Coumarins and Other Polycyclic (Hetero)aromatic Dyes

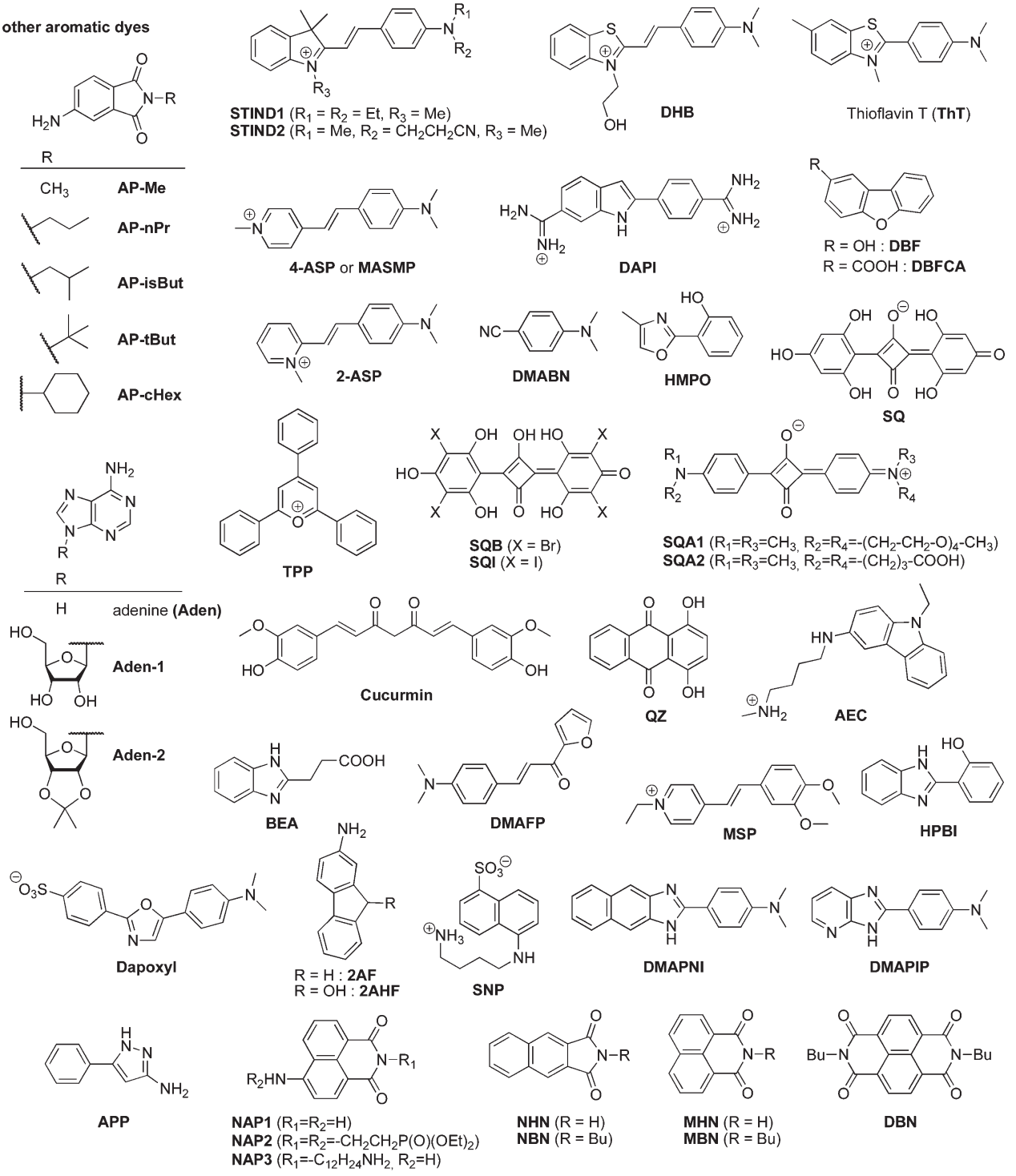


and significant fluorescence enhancement or quenching have been accurately quantified in order to provide guidance to the reader in regard to the choice of dyes for related studies. Therefore, while complexation studies of macrocycles with drugs have been performed,[34−38] sometimes even *via* fluorescence spectroscopy,[39] these have been, with few exceptions, largely excluded from this review.

The structure of the review will be such that we will first summarize prototypal dyes with their properties and applications and then detail the different macrocyclic hosts, discuss the

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Scheme 4. Miscellaneous Dyes (Part 1)



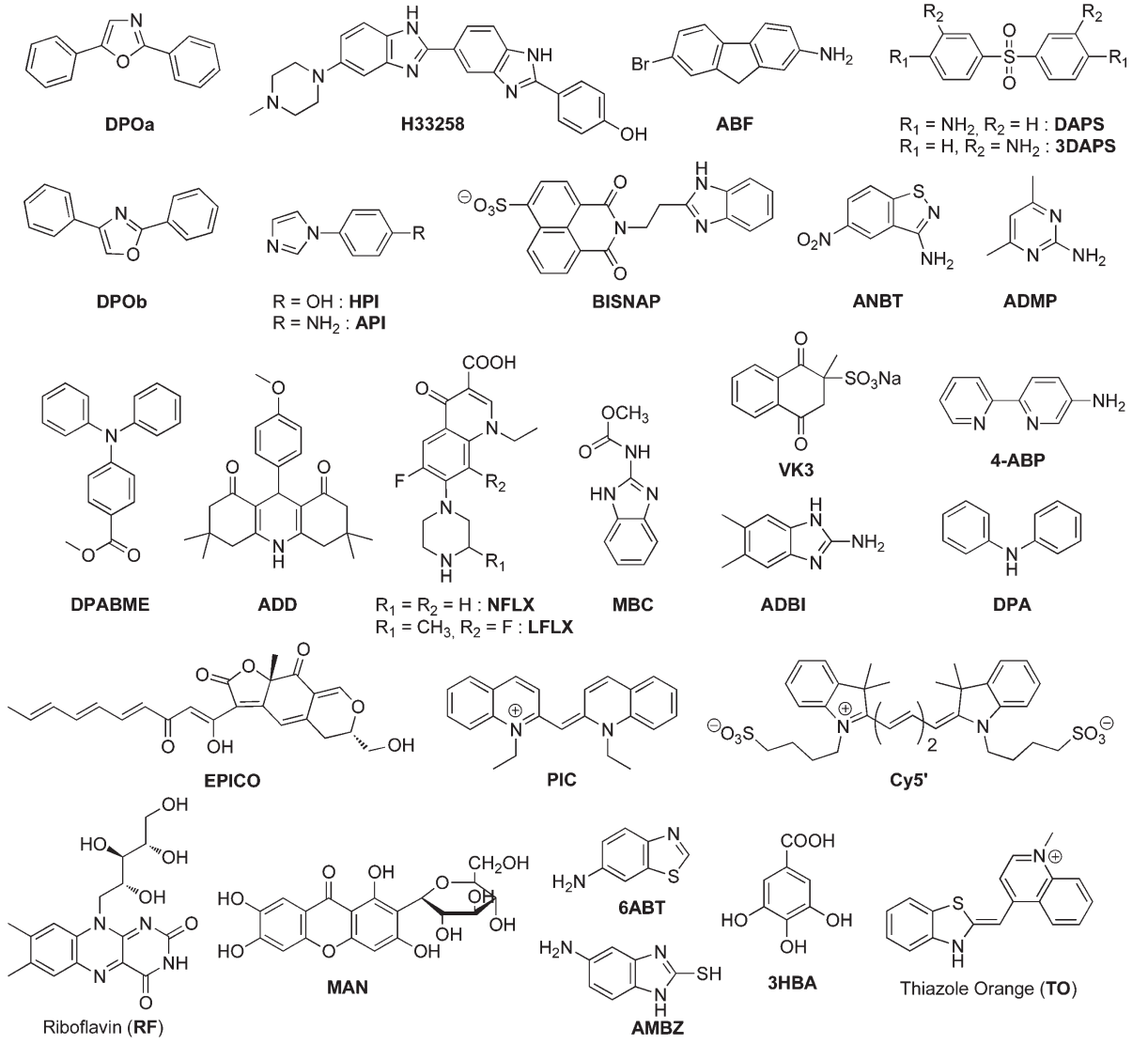
photophysical effects accompanying host/guest complexation, and conclude with diverse applications.

2. WATER-SOLUBLE FLUORESCENT DYES

Dyes are commonly grouped into acridines, xanthenes, quinone-imines, arylmethanes, and nitro/azo dyes. The *fluorescent* dyes that have been found to serve as guests for macrocyclic hosts in aqueous media are compiled in Schemes 1−5. The acridine dyes include acridine orange (AO), acridine yellow (AY), and proflavin (PF). The reviewed xanthene dyes are subcategorized into fluorenes [*e.g.*, acridine red (AR), pyronine (PY), pyronine Y (PYY), pyronine B (PYB), rhodamine B (RhB), rhodamine 123 (R123), tetramethylrhodamine (TMR), kiton red S (KRS), rhodamine B benzyl ester (RhBBE), butyl rhodamine B (BRB), rhodamine

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Scheme 5. Miscellaneous Dyes (Part 2)



6G (R6G), and rhodamine 800 (Rh800)] and fluorones [*e.g.,* erythrosine sodium (ES), fluorescein sodium (FS), salicyl fluorone (SAF), tetrachlorotetraiodofluorescein (TCTIF), and tetrachlorofluorescein (TCF)]. The most popular quinone-imine dyes include azines [*e.g.,* safranine T (ST) and neutral red (NR)], oxazines [*e.g.,* nile blue (NiB), nile red (NiR), oxonine (OX), oxazine 1 (OX1), Meldola's blue (MDB), and brilliant cresyl blue (BCB)], and thiazins [*e.g.,* thionine (TH), azure A (AZA), methylene blue (MB), toluidine blue (TB), and new methylene blue (NMB)]. Auramine O (AuO) and bisphenol A (BPA) are classified as arylmethane dyes. Coumarin dyes such as 7-methoxycoumarin (7MC), coumarin 153 (C153), coumarin 480 (C480), coumarin 460 (C460), HCD-1, HCD-2, HCD-3, 4PBTC, 6-methylcoumarin (6MeC), coumarin 6 (Cou-6), and osthole (OST) are also included. Alkaloid dyes include berberine (BE), coptisine (CP), coralyne (COR), sanguinarine (SA), palmatine (PLM), and dehydrocorydaline (DHC), which have been discussed as well. Among the miscellaneous dyes fall polycyclic aromatic hydrocarbon derivatives [*e.g.,* 1-anilinonaphthalene-8-sulfonic acid (1,8-ANS), 2-anilinonaphthalene-6-sulfonic acid (2,6-ANS), 2-(*p*-toluidinyl)naphthalene-6-sulfonic acid (2,6-TNS), 6-propionyl-2-dimethylaminonaphthalene (PRODAN), 2,2′-binaphthol (*R*-BOH and *S*-BOH), dansylcholine (DANSCh), 2-aminoanthracene (AA), pyrene (Pyr), pyrene-3-carboxaldehyde (Pyr-CHO), 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS), pyridinopyrene (PP), 2-(4-phenylboronic acid)-1-pyrenemethamide (APB), and other naphthalene derivatives (HAN, DMN, DEN, 2NC, 23NC, 27NC, HN12, and SNP)], polycyclic heteroaromatic dyes [*e.g.,* acridizinium (ADZ), 9-aminoacridizinium (AADZ), *N*,*N*′-dimethyl-2,7-diazapyrenium (Me_2DAP), diquat (DQ), diazaphenanthroline (DPT), lumichrome (LC), 2-quinoxalinyl-phenoxathiin (QP), lucigenin (LCG), phenoxathiins (ALP, KEP, CAP), and tetramethyl benzobis(imidazolium) (MBBI)], and other dyes with aromatic character [*e.g.,* Dapoxyl, 4′,6-diamidino-2-phenylindole (DAPI), *p*-(*N*,*N*-dimethylamino)benzonitrile (DMABN), 2,4,6-triphenylpyrylium (TPP), squaraine derivatives (SQ, SQB, SQI, SQA1, and SQA2), styryl derivatives (2-ASP, 4-ASP, MSP),

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Table 1. Photophysical Properties of Free Dyes (See Also Figure 1 for an Overview)

dye	λ_{ex}/nm	$\lambda_{max,f}$/nm	Φ_f	τ_f/ns	conditions	ref
			Acridine Dyes (Scheme 1)			
PF	400	516			pH 7.0	160
			0.34		pH 7.0	51
	400	514	0.44	5.0	pH 6.9 (phosphate buffer)	52
AO	435	550	0.055	6.2	pH 12.0	50
	492	535	0.041	1.7	pH 7.0	50
	450	535	0.25	1.7	pH 6.9 (phosphate buffer)	52
AY	444	508		5.05	H_2O	161
	436	517	0.47		EtOH	162
			Xanthene Dyes (Fluorenes) (Scheme 1)			
PY			1.00		H_2O	163
	513			2.3/5.28	H_2O	67
PYB	553	573	0.36	1.17	pH 3.4−4.0	58
	551	566	0.40		H_2O	57
PYY	547	567	0.47	1.76	pH 3.4−4.0	58
	546	558	0.35		H_2O	57
RhB	554	576	0.50		acidic EtOH	164
		568		1.52	H_2O (acidic)	61
	558	577	0.24	1.58	H_2O (acidic)	165
		583		1.68	H_2O (neutral)	61
	554	573	0.31	1.75	H_2O (neutral)	165
	563	589	0.55		acidic EtOH−glycerol (9:1)	166
	556	583	0.75		alkaline EtOH−glycerol (9:1)	166
	554	578	0.32	1.5	H_2O	167
R123	500	525	0.83	4.19	H_2O	71
TMR	553	577	0.28	2.15	H_2O	71
KRS	565	586	0.27	1.5	H_2O	167
R6G	530	553	0.95		ethanol	164
		558	0.95	4.08	H_2O	61
	526	551	0.59	3.95	H_2O	165
	528	552		4.2	pH 8.7 (tris buffer)	85
	488−546	565	0.76−0.81		H_2O	162
			Xanthene Dyes (Fluorones) (Scheme 1)			
FS	494	518		4.1	H_2O	85
	487	523	0.93	7.6	pH 12.5	66
		520	0.93−0.95	4.16	pH 11.0	61
			0.95		pH 11.0	64
				4.3	pH 11.0	168
	488	533	0.90		pH 13.0	162
TCTIF	550	568		0.1	pH 8.7 (tris buffer)	85
				0.085	H_2O	168
ES			0.07	0.5	pH 12.5	66
		548		0.095	pH 11.0	168
			Quinone-imine Dyes (Azines) (Scheme 2)			
NR	452	625		0.7	pH 9.0	75
	450	637	0.02		pH 8.1	76
	535	637	0.02		pH 5.3	76
	475	609	0.004		pH 7.5 (phosphate buffer)	169
ST	523	577			pH 7.2	170
			Quinone-imine Dyes (Oxazines) (Scheme 2)			
NiB	636	702	0.27		EtOH	92
	628	667		1.42	EtOH	40

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Table 1. Continued

dye	λ_{ex}/nm	$\lambda_{max,f}$/nm	Φ_f	τ_f/ns	conditions	ref
	635	674	0.01		H_2O	40
	457	556			pH 1.0	40
	522	668			pH 11.0	40
NiR	600	660		0.42	H_2O	86
	580	612/650		2.8/0.9	pH 8.7 (tris buffer)	85
	591	657			H_2O	88
	550	665	0.018	0.65	H_2O	87
	559	629	0.57	3.65	EtOH	90
OX			1.00	3.2	H_2O	163
OX1	654	671			pH 6.5 (phosphate buffer)	171
	647	693	0.11		EtOH	92
BCB	626	670			HMTA buffer	172
MDB	567	652			H_2O	173
	540	568			EtOH	40
			Quinone-imine Dyes (Thiazines) (Scheme 2)			
TH	598	623			H_2O	174
	600	610	0.05		H_2O	97
				0.320		175
				0.360	H_2O	95
AZA	633	660	~0.05		H_2O	95
MB	665	685		0.370	H_2O	95
	665	682		0.358	H_2O	97
		686	0.02	0.345	H_2O	94
				0.379	H_2O	96
				0.380	H_2O	176
				0.365	H_2O	177
	633	710	0.04		EtOH	162
			Arylmethane Dyes (Scheme 2)			
AuO	430	495			pH 7.0	178
	435	485	0.0045	0.092	1-decanol	98
	428	485	0.00009	<0.02	pH 7.4 (phosphate buffer)	98
			Azo Dyes (Scheme 2)			
DBO	365	430	0.2	420	H_2O	100
DBO-Amine	370			670	D_2O	179
			Coumarin Dyes (Scheme 3)			
C153		554	0.15	1.46	H_2O	180
	430	549	0.12		H_2O	120
C480	396	489	0.66	5.9	H_2O	120
7MC	323	390	0.05		MeOH	122
	320	395			H_2O	181
Cou-6	458	505	0.78		EtOH	182
	469	508	0.59	3.3	50% EtOH	120
6MeC	320	411	0.008	<0.1	H_2O	183, 184
HCD-1	338	440	0.036	<0.5	pH 5.4	185
HCD-2	316	446	0.0022	<0.5	pH 5.4	185
HCD-3	302	349	0.0073	<0.5	pH 5.4	185
			Miscellaneous (Polycyclic Aromatic Hydrocarbons) (Scheme 3)			
1,8-ANS	352	523	0.003	0.25	H_2O	125
PRODAN	364	531		2.1	H_2O	126
R-/S-BOH	336	355	0.01−0.016	2.4−3.4	H_2O	186
HN12	375	460	0.007	0.09/0.59	H_2O	187
HPTS	404	442	1	4.8	pH 2.0	132

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Table 1. Continued

dye	λ_{ex}/nm	$\lambda_{max,f}$/nm	Φ_f	τ_f/ns	conditions	ref
	461	514	1	5.3	pH 10.0	132
DANCh	340	572			pH 6.9	188
		577	0.07		pH 7.2	189
			Miscellaneous (Polycyclic Heteroaromatic Dyes) (Scheme 3)			
ADZ	396	404	0.33	6.0	pH 7.0	134
AADZ	385	507	0.19	14.0	H_2O	133
BE	422	556	0.00047		D_2O	190
LCG	368	485	0.50	25.3	H_2O	191
MBBI	287	328	0.91		H_2O	192
QP	360	484	0.05		DMF/H_2O (1:9)	193
			Miscellaneous (Other Aromatic Dyes) (Schemes 4 and 5)			
Dapoxyl	348	584	0.04		H_2O	137
TPP	406	469	0.25	2	pH 4.7 (acetate buffer)	194
SQ	584	595	0.002	0.085	pH 8.6	141
SQB	613	630	0.002		10% (v/v) EtOH−H_2O	195
SQI	617	634	0.0009		10% (v/v) EtOH−H_2O	195
SQA1	645	674	0.018	0.16	10% (v/v) EtOH−H_2O	195
SQA2	647	673	0.015		10% (v/v) EtOH−H_2O	195
4-ASP	445	615	≤0.001		pH 7.0	150,153
	452	613		0.011	H_2O	151
	476	593	0.003		MeOH	196
	450	581		0.04	H_2O	155
2-ASP	432	573	0.018	0.81	H_2O	197
	463	572	0.003		MeOH	196
HPMO	314	350/425		0.22/2.64	pH 6.0	144
NFLX	336	410	0.12	1.5	pH 7.4	198
2AF	315	377	0.20	2.1	pH 8.0	199
ThT	412	489		3.76	H_2O	200
	412	493	0.0003		pH 7.7 (tris buffer)	145
NAP3	375	535	0.049		pH 4.5	201
			0.036		pH 6.0	
MHN	340	384	0.032	0.26	EtOH	143
DBN	380	388	0.001		CH_3CN/H_2O (1:1)	202
DMAPNI	356	437		1.86	1% MeOH in H_2O	203
DMAPIP	386	451	0.0065		pH 4.0	204
	345	451	0.042	0.18	pH 9.0	
3DAPS	228/307	333/411		1.08	pH 6.0	205
RF	460	537		1.94	pH 7.0	206
DMABN	297	361/550	0.0007	0.31	H_2O	207
DBF	310	352	0.079		pH 7.0	208
	340	443	0.035		pH 13.0	208
DBFCA	288	371	0.140		pH 2.0	209
	286	333	0.073		pH 10.0	209
2AHF	296	398		2.01	H_2O	210
DMAFP	446	555	0.0032		H_2O	211
AEC	364	458	0.76		pH 7.5	212
ABF	288	376		2.99	H_2O	213
HPBI	295	320	1.8		pH 4.0	214
	289	313	1.8/3.0		pH 7.0	
ADMP	284	342	0.048	4.37	H_2O	215
DPABME	331	420		1.00/5.47	H_2O	216
ADBI	284	313		0.28	H_2O	217
ANBT	347	412		1.34	pH 6.8	218

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Table 1. Continued

dye	λ_{ex}/nm	$\lambda_{max,f}$/nm	Φ_f	τ_f/ns	conditions	ref
BISNAP	338	395	0.031		pH 3.5	219
			0.005		pH 7.0	
H33258	337	508	0.015	0.20	pH 7.4 (tris buffer)	158
	337	490	0.02		pH 7.0 (phosphate buffer)	159
	338	502	0.02	2.41	pH 7.0	157
	338	479	0.01	1.56	pH 7.0 (phosphate buffer)	220
DAPI	341	496	0.019	0.16	pH 7.4 (tris buffer)	158
EPICO	435	533	0.008	0.3/1.16	H_2O	221
AMBZ	303	377		3.96	pH 6.9	222
6ABT	282	426		0.65	pH 7.0	223
Cy5′	642	660	0.17	0.63	H_2O	71
ADD	385	440	0.08	0.71	H_2O/MeOH (96/4)	224

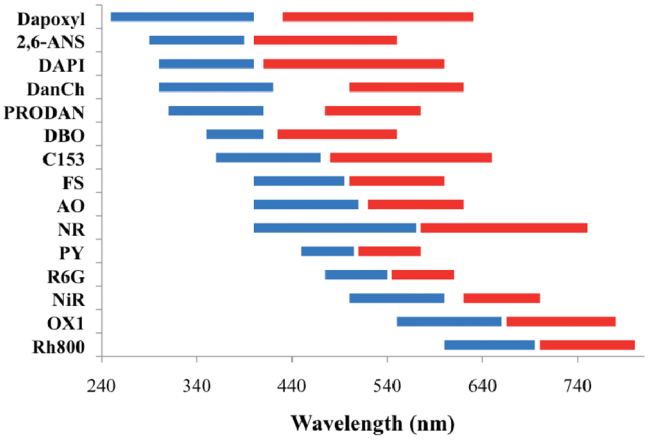


Figure 1. Absorption (blue bars) and fluorescence (red bars) ranges of several important dyes.

benzimidazoles (HPBI, BEA, ADBI, MBC, H33258, BISNAP), 2-styrylindolium dyes (STIND1, STIND2), 2-(4-dimethylaminostyryl)-3-(2-hydroxyethyl)benzothiazolium (DHB), *N*-(4-hydroxylphenyl)imidazole (HPI), *N*-(4-aminophenyl)imidazole (API), dibenzofuran-2-carboxylic acid (DBFCA), 2-dibenzofuranol (DBF), lomefloxacin (LFLX), norfloxacin (NFLX), Cucurmin, aminophthalimide (AP) derivatives, naphthalimide derivatives (NAP1, NAP2, NAP3, MHN, MBN, DBN, NHN, NBN), aminofluorenes (2AF, 2AHF), thioflavin T (ThT), thiazole orange (TO), adenine derivatives (Aden, Aden-1, Aden-2), 2-(2′-hydroxyphenyl)-4-methyloxazole (HMPO), 3-amino-5-phenylpyrazole (APP), 3-(4′-dimethylaminophenyl)-1-(2-furanyl)prop-2-en-1-one (DMAFP), 3-*N*-[4-(methylamino)butyl]-9-ethylcarbazole (AEC), 2-(4′-*N*,*N*-dimethylamino)phenylimidazo[4,5-*b*]pyridine (DMAPIP), 2-(4′-*N*,*N*-dimethylaminophenyl)-1*H*-naphth[2,3-*d*]imidazole (DMAPNI), 2,4- and 2,5-diphenyloxazole (DPOa and DPOb), 2-amino-7-bromofluorene (ABF), vitamin K3 (VK3), diphenylamine (DPA), 2-amino-4,6-dimethylpyrimidine (ADMP), quinizarin (QZ), *p*-(*N*,*N*-diphenylamino)benzoic acid methyl ester (DPABME), 4,4′-diaminodiphenylsulfone (DAPS), 3,3′-diaminodiphenylsulfone (3DAPS), 3-amino-5-nitrobenzisothiazole (ANBT), epicocconone (EPICO), cyanine derivatives (PIC and Cy5′), 3,4,5-trihydroxybenzoic acid (3HBA), riboflavin (RF), mangiferin (MAN), an acridinedione dye derivative (ADD), 6-aminobenzothiazole (6ABT), 5-amino-2-mercaptobenzimidazole (AMBZ), and 4-aminobipyridine (4-ABP)]. We will also discuss the category of azo dyes, which along with nitro dyes are generally nonfluorescent, with the singular exception of the 2,3-diazabicyclo-[2.2.2]oct-2-ene chromophore (DBO and DBO-Amine).

As a reference point, the photophysical properties of the most important dyes are provided in Table 1 in their uncomplexed form. The absorption and fluorescence spectral ranges of several important dyes are featured in Figure 1 for quick reference. Selected examples will also be discussed briefly in the following with regard to their photophysics and applications, while comprehensive reviews beyond the context of host/guest complexes can by found in the literature.[40−45]

Acridine Dyes

The structure of AO is based on the acridine heterocyclic skeleton. The dye has found wide application as a fluorescent probe for the differentiation between DNA and RNA and as an agent for staining of cellular structures.[46−48] Furthermore, it has been applied for probing solvent relaxation dynamics in micelles.[49] The photophysical properties of AO show a significant dependence on the pH.[50] The pK_a value of the dye is reported between 9.5 and 10. Thus, at physiological pH around 7, the dye is exclusively present in its protonated form, which shows fluorescence emission with a maximum at 535 nm and a Stokes shift of *ca.* 40 nm. In the neutral form, the fluorescence maximum undergoes a red shift by *ca.* 15 nm; however, the Stokes shift increases to *ca.* 110 nm. The fluorescence quantum yield of the dye is low (Φ_f = 0.041 at pH 7), which, on the other hand, is compensated by the rather large absorption coefficient (ε_{492} *ca.* 73000 M^{-1} cm^{-1}). PF is another acridine dye, lacking the methyl substituents of AO. It has a higher reported fluorescence quantum yield at pH 7 (Φ_f = 0.34−0.44),[51,52] and like AO, it is also used as a DNA intercalator.[52−54]

Xanthene Dyes

Xanthene dyes are generally divided into fluorenes and fluorones. The fluorene dyes, which are discussed in this review, can be subgrouped into pyronins and rhodamines. AR, PYY, and PYB are structurally distinguished from the parent PY by alkyl substitution at the aromatic nitrogens. AR has been used in fluorescent labeling of blood platelets and leukocytes.[55] In combination with methyl green, PYY finds extensive use for differential dichromatic staining of nucleic acids: PYY stains RNA red, while methyl green stains DNA green.[56] PYY and PYB show yellow emission with small Stokes shifts (*ca.* 20 nm) and

moderate fluorescence quantum yields ($\Phi_f \approx 0.4-0.5$).[57,58] Both dyes have been applied recently for the determination of kinetic parameters of host/guest complex formation with β-CD by using fluorescence correlation spectroscopy.[59]

Rhodamines (e.g., RhB, R6G, Rh800) constitute another subgroup of fluorene dyes. These dyes find general application for coloring of textiles, as laser dyes, and in fluorescence microscopy. Furthermore, rhodamines have potential as singlet oxygen sensitizers.[60] Rhodamines belong to the dyes with a fluorescence quantum yield of practically 1 ($\Phi_f = 0.95$ for R6G in water).[61] They fluoresce with maxima around 550−580 nm and are characterized by small Stokes shifts (*ca.* 20 nm).[61]

Fluorones are derived from the fluorescein (FS) parent structure. FS is a well-known pH indicator, which is based on the existence of four different protonation states (monocation, neutral, and mono- and dianion), related to each other by pK_a values of 2.14, 4.45, and 6.80.[62] In basic solution (pH 11) the dye has a fluorescence maximum at 520 nm and an emission quantum yield near 1 ($\Phi_f = 0.93-0.95$).[63,64] There exist several dyes, which are derived from fluorescein by introduction of halogen substituents at the xanthene skeleton: erythrosine sodium (ES), tetrachlorotetraiodofluorescein (TCTIF, also known as rose bengal), and eosin Y. The substitution with heavy atoms yields very efficient intersystem crossing (Φ_{ISC} = 0.69 for ES and *ca.* 1 for TCTIF versus 0.03 for FS), which, on the other hand, reduces the fluorescence quantum yield of these dyes drastically ($\Phi_f < 0.1$).[65,66] Triplet-excited TCTIF is an efficient singlet-oxygen sensitizer [$\Phi(^1O_2) = 0.75$ in water].[65]

It is noteworthy that acridine, xanthene, and phenothiazine dyes show, in general, a strong tendency for the formation of aggregates in aqueous solution.[67−70] This phenomenon often has dramatic consequences for the photophysical characteristics of these compounds, as expressed by variations in their absorption and fluorescence spectra as well as their emission quantum yields. Depending on the equilibrium constant for aggregate formation, this may already happen for micromolar concentrations of the dye.[67,70,71] The formation of these aggregates can be suppressed by dye complexation with macrocyclic hosts (see section 4).

Quinone-imine Dyes

The herein discussed examples for this class of dyes can be divided into three groups: azines, oxazines, and thiazines (see Scheme 2). Neutral red (NR), an azine dye, is used for staining biological tissues and has also found application as an intracellular pH indicator in the pH range 6−8.[72] The dye shows emission from the locally excited (LE) or twisted internal charge transfer (TICT) state, depending on the polarity of the solvent medium and the protonation state.[73,74] In its unprotonated form in water (at pH 8−9), the absorption maximum is at 452 nm and the emission maximum is at 625 nm.[75] The resulting large Stokes shift of *ca.* 170 nm is in accordance with the charge transfer character of the emissive state. In the protonated form (water at pH 5) the LE state prevails, which is accompanied by a red-shifted absorption spectrum (λ_{max} = 535 nm) and a smaller Stokes shift (*ca.* 100 nm). The fluorescence quantum yield is reported as Φ_f *ca.* 0.02 for both the protonated and the neutral form.[76]

Meldola's blue (MDB), nile red (NiR), nile blue (NiB), and oxazine 1 (OX1) are all oxazine dyes. MDB was one of the first discovered fluorescent examples of the class of oxazine dyes. This compound has found application as pigment in paints, textiles, or paper. On the other hand, MDB is encountered in redox-sensing systems for glucose, hydrogen peroxide, or NADH.[40] NiR is far more extensively used than MDB and has found wide application as a lipophilic stain[77,78] as well as a microenvironmental probe for zeolites,[79,80] Langmuir−Blodgett films,[81] and micellar structures.[82] For example, 2-hydroxy-NiR has been used to probe micelle microenvironment and micelle formation of ionic liquids.[83,84] In water, NiR absorbs with a maximum around 580−600 nm and emits at *ca.* 650 nm.[85−88] This rather red-shifted fluorescence makes this dye a good candidate for biolabeling applications, as the absorption of most biomolecules does not show significant overlap with the dye's emission spectrum. The fluorescence is strongly solvent-dependent.[88,89] For example, in acetone the emission is *ca.* 50 nm blue-shifted with respect to water. The fluorescence in water is rather weak (Φ_f *ca.* 0.02),[87] which is most likely caused by self-quenching effects due to dye aggregation and hydrogen-bonding-induced radiationless deactivation.[40,90] However, the fluorescence quantum yield can reach significant values in organic solvents and has been reported as Φ_f *ca.* 0.7 in neat dioxane and 0.57 in ethanol.[78,90] The electronic structure of NiB is comparable with that of NiR, both having a diethylamino electron donor substitution at the 9-position. Therefore, the excited-state charge-transfer character is preserved also in NiB, giving rise to similar solvatochromic behavior as for NiR: a red-shifted emission in media of high polarity.[91] Because NiB bears a permanent positive charge, it has the advantage of being more water-soluble than NiR. OX1 is used as a laser dye; in ethanol, it shows a Stokes shift of 46 nm and a moderate fluorescence quantum yield ($\Phi_f = 0.11$).[92] One reason for this observation is the rather efficient deactivation by internal rotation of the amino groups. Support for this argument has been drawn from the increased emission quantum yield in solvents of higher viscosity, i.e., $\Phi_f = 0.19$ in ethylene glycol.[92]

Thionine (TH) and methylene blue (MB) are representative dyes of the thiazine subgroup of quinone-imine dyes. For the example of MB the application spectrum includes textile coloring, cellular staining, use as redox indicator and sensitizer in photodynamic antimicrobial therapy.[93] It is also known to intercalate into DNA.[94−96] The dyes are characterized by emissions above 600 nm and relatively small Stokes shifts (*ca.* 20 nm). In water, TH and MB show fluorescence quantum yields equal to 0.05 or smaller.[94,97] The fluorescence lifetimes are reported between 0.3 and 0.4 ns. Self-aggregation of MB in aqueous solution is a commonly encountered phenomenon, yielding a nonfluorescent dimer.[94] The excited-state interactions of TH with mono- and polynucleotides, supposedly *via* photoinduced electron transfer, have been investigated as well.[95]

Arylmethane Dyes

Auramine O (AuO) has a very low fluorescence quantum yield in protic solvents of low viscosity ($\Phi_f < 0.0001$ in water) and lifetimes in the range of a few picoseconds ($\tau_f < 20$ ps), very typical for arylmethane dyes.[98] The main excited-state deactivation pathway is connected to internal rotation of the *N*,*N*-dimethylaniline residues.[98,99] Thus, nonradiative deactivation dominates and leads to weak emission. However, solvents such as 1-decanol or glycerol slow down the internal rotation due to the increased microviscosity, and, as a result, the emission properties are somewhat improved ($\Phi_f = 0.0045$ in 1-decanol).[98,99] The same applies for the complexation of AuO by biomolecules such as proteins and DNA, but the

fluorescence enhancements are strongly dependent on the binding mode.[98]

Azo Dyes

Generally, azo dyes are nonfluorescent due to efficient *cis*–*trans* isomerization around the N=N bond. However, if the azo motif is inserted in a rigid structure, and if intersystem crossing is suppressed, then fluorescence can be observed. This is the case for DBO. Its absorption spectrum shows the typical weak absorption due to the n,π^* transition (ε < 200 $M^{-1}cm^{-1}$ in most solvents) at around 365 nm (for water).[100,101] The rather broad emission has a maximum around 430 nm, and the fluorescence quantum yields are moderate, e.g., Φ_f = 0.2 in water.[100,102] However, the real advantage of this fluorophore is its exceptionally long fluorescence lifetime, which can reach up to 700 ns in acetonitrile and 420 ns in water, both under deaerated conditions.[100,101] On the other hand, in aerated water, a still very long lifetime of 325 ns is retained. From a quenching–mechanistic point of view, DBO is an all-rounder: it is involved in hydrogen transfer with alkanes, haloalkanes, aromatic systems, phenols, and even water and alcohols, and it shows exciplex-induced quenching with electron-donating amines.[103,104] Both mechanisms have been shown to involve a conical intersection, leading to chemically unproductive fluorescence quenching.[105,106] The dye has found numerous applications, among them as probe for antioxidant reactivity,[107–109] as an acceptor in Förster resonance energy transfer (FRET) experiments,[110,111] biopolymer folding,[112–114] enzyme assays,[115,116] supramolecular dynamics,[102,117] and properties of host/guest complexes,[118] and in micellar systems.[119]

Coumarin Dyes

The parent coumarin is essentially nonfluorescent. However, substitution in the 7-position with electron-donating groups yields fluorescent derivatives (Scheme 3). The C153 dye contains an electron-donating amino function in the 7-position, which confers intramolecular charge-transfer character to the fluorescence emission. This is corroborated by the observed solvatochromic effects. For example, upon going from the nonpolar cyclohexane ($\lambda_{max,f}$ = 455 nm) *via* the polar acetonitrile ($\lambda_{max,f}$ = 521 nm) to water ($\lambda_{max,f}$ = 549 nm), a strong red shift of the fluorescence maximum by *ca.* 100 nm is observed.[120] A similar trend, albeit less pronounced, is observed in the absorption spectra of C153 in these solvents.[120] The fluorescence quantum yield of C153 in protic solvents such as water or ethanol is moderate (Φ_f < 0.4) but reaches higher values in nonhydroxylic organic solvents, e.g., acetonitrile (Φ_f = 0.56), and is almost unity in the nonpolar cyclohexane (Φ_f = 0.90).[120] It has been demonstrated that the photophysical properties of C153 are controlled by the S_1–S_0 energy gap.[121]

On the other hand, the 7MC dye, which contains an electron-donating methoxy substituent in the 7-position, shows comparably small fluorescence quantum yields (Φ_f = 0.05 in methanol) and only minor shifts of the absorption and fluorescence band maxima upon going from benzene to acetonitrile.[122] These observations support the occurrence of less charge transfer than for C153.

Coumarin-6 (Cou-6) is a laser dye with similar red-shifted absorption and fluorescence spectra like C153. However, the fluorescence quantum yield of this dye in protic solvents (e.g., 50% ethanol) is higher than that observed for C153 (Φ_f = 0.38 and 0.59 for C153 and Cou-6, respectively).[120] C480, another frequently used coumarin laser dye, has slightly blue-shifted absorption and fluorescence maxima as compared to C153 and Cou-6, but the fluorescence quantum yield in 50% ethanol reaches 1.[120] The differential effects of the substitution pattern (donor/acceptor properties) and the rotational freedom of the amino substituent play a key role in the partition between radiative versus nonradiative excited-state deactivation channels, where intramolecular charge transfer states, including twisted ones, may be important.

Polycyclic Aromatic Hydrocarbons

The textbook examples for polycyclic aromatic hydrocarbon dyes include naphthalene, anthracene, pyrene, or perylene. Also, donor–acceptor-substituted aromatic hydrocarbons fall in this category. Some of the most prominent examples with such electronic structure are 1,8-ANS, 2,6-ANS, 2,6-TNS, PRODAN, and the dansyl-based chromophores (e.g., DANSCh). These fluorophores are considered to involve intramolecular charge-transfer processes in their photophysics and, thus, show pronounced solvatochromic effects.[123–128] Typical for these dyes are the large Stokes shifts, which reach values between 150 and 200 nm. For 1,8-ANS, the fluorescence quantum yield in water is very small (Φ_f = 0.003) but increases to Φ_f = 0.41 in ethanol as solvent.[125] In the same medium, PRODAN shows a quantum yield of Φ_f = 0.71.[129] These dyes have found wide applications as biological probes for protein environments.[126,130,131] The dansyl chromophore can be easily derivatized with amino acids (for example as DANSCh) and is used, among others, as a tag in bioanalytical applications. The fluorescence maxima of these dyes are above 500 nm, which is an additional surplus in terms of a very selective signal read-out.

Akin to many hydroxyarenes, the acidity of HPTS is enhanced in the excited state. This opens the mechanistic possibility of excited-state proton transfer, which comes into play for this dye.[132] The neutral form, which exists in very acidic solution (pH = 2), shows its fluorescence maximum at 442 nm. The corresponding anion (basic solution, pH = 10) has its emission maximum at 514 nm. Remarkably, the total emission quantum yield (sum of neutral OH form and anionic O^- form) is practically 1.

Polycyclic Heteroaromatic Dyes

Acridizinium salts such as ADZ or AADZ belong to this group and have recently been found to display interesting fluorescence properties.[133,134] The parent acridizinium cation (ADZ) emits around 400 nm with a moderate quantum yield (Φ_f = 0.33) and has a small Stokes shift (8 nm). On the other hand, the amino-substituted AADZ can also be viewed as containing the structural motif of cyanine dyes.[133] This green-emitting fluorophore has a large Stokes shift (*ca.* 120 nm in water), typical for push–pull π-conjugated systems. The absorption and fluorescence spectra show moderate solvatochromic effects (e.g., fluorescence maximum at 497 nm in acetic acid and at 516 nm in dimethylsulfoxide). The fluorescence quantum yield of AADZ in water is moderate (Φ_f = 0.19) but increases to Φ_f = 0.72 in acetic acid.[133] AADZ has been shown to intercalate into DNA,[135] which is accompanied by fluorescence quenching.[133]

Other Aromatic Dyes

Finally, some examples of other aromatic dyes, which do not fall unambiguously into any of the other above-mentioned groups, are briefly discussed (see Schemes 4 and 5). Dapoxyl is an environment-sensitive dye, which has recently received much attention.[136,137] Its solvatochromic properties are

reflected in a red shift by 144 nm upon changing from neat acetonitrile to 1:9 acetonitrile/water. The mechanistic foundation for these observations is an intramolecular charge transfer process from the *N*,*N*-dimethylanilino group to the sulfonyl moiety. Once more, the Stokes shift of *ca.* 240 nm is in line with this rationalization. The dye has been applied, for instance, as a fluorophore in a protein kinase assay.[138]

DMABN is rightfully considered an archetypal charge-transfer dye, showing dual fluorescence originating from the locally excited state (short-wavelength emission) and the intramolecular charge-transfer state (long-wavelength emission).[139,140] The resulting solvatochromic properties render this dye an interesting and widely applied environmentally sensitive fluorescent probe and an attractive candidate for the study of excited-state charge-transfer phenomena.

The squaraine dye SQ shows pH-dependent photophysical properties.[141] The only (but weakly) fluorescent form is the anion resulting from deprotonation of the dye (pH 7.5−9.5). Of special interest are the strongly red-shifted absorption and fluorescence maxima (580−600 nm). In water, the anionic form is weakly fluorescent ($\Phi_f \leq 0.002$), which is somewhat improved in methanolic solution ($\Phi_f = 0.02$). Squaraine dyes have found application, in particular, in near-infrared emitting materials and as chemosensors.[142]

Many naphthalimides such as the parent compound, MHN, or its 4-amino derivative, NAP1, are practically insoluble in water. MHN is sufficiently soluble in ethanol for performing photophysical studies (see data in Table 1) and shows rather small fluorescence quantum yields and lifetimes in most organic solvents.[143] The same applies to bisimides such as DBN. NAP1 and therefrom derived compounds (such as the water-soluble derivative NAP3) show markedly red-shifted absorption and fluorescence spectra, which express the pronounced charge transfer character in the excited state.

HMPO is a dye with an intramolecular hydrogen bond between the phenolic OH group and the oxazole nitrogen. In the excited state, intramolecular proton transfer occurs.[144] In nonpolar solvents, such as 3-methylpentane, an emission at 470 nm results. This corresponds to a Stokes shift of 150 nm. In protic solvents, such as water, intermolecular excited-state proton transfer proceeds. Hence, a dual fluorescence of the locally excited solvated structure of the dye (350 nm) and its phenolate anion (425 nm) is observed. Intuitively, in aqueous solution, the emission properties are pH-dependent. The dye may be a promising probe for biological structures such as proteins and has been tested for human serum albumin.[144]

ThT (thioflavin T) is a cationic benzothiazole dye, which shows a large fluorescence increase in the presence of amyloid fibrils.[145,146] This has been used to detect these biological structures in tissues and proteins. The mechanistic background of this fluorescence enhancement is not entirely clear, but it has been speculated that the hindered rotation around the benzothiazole-dimethylaniline axis in confined environments is a determining factor.[147,148] Furthermore, ThT is known to interact with DNA.[149]

2-ASP and 4-ASP are styrylpyridinium dyes with electron donor−acceptor architecture. Expectedly, these dyes show polarity-dependent fluorescence.[150] Internal conversion (for example by rotational movements) has been discussed as an excited state deactivation mechanism.[150−152] 4-ASP binds to the minor groove of DNA, which is accompanied by fluorescence enhancement.[153] Furthermore, styrylpyridinium dyes are known as voltage-sensitive dyes for probing lipid membranes.[154] The fluorescence of 4-ASP in the presence of surfactants or in reverse micelles has been studied as well.[151,155]

H33258 is a bisbenzimidazole dye which is widely applied as a DNA stain.[156] The fluorescence maximum (around 480−500 nm) is strongly dependent on pH and on the microenvironment of the dye.[157] At pH 7 the dye is only very weakly fluorescent, but upon interaction with DNA, a strong fluorescence enhancement is observed.[158,159] The rigidfication of the dye bound to DNA is thought to be responsible for this "light-up" behavior.

3. WATER-SOLUBLE MACROCYCLES

3.1. Cyclodextrins

The classical macrocycles, which have been extensively investigated for their complexation properties of fluorescent dyes, are the naturally occurring cyclodextrins (CD), α-, β-, and γ-CD, cyclic oligomers composed of 6, 7, and 8 α-D-glucose units (Scheme 7).[8,226] They are uncharged but possess a hydrophobic inner cavity as well as a primary ("lower" or narrower) and secondary ("upper" or wider) hydroxyl group rim, which provides additional hydrogen bonding motifs for the binding of organic guests. Their common schematic representation is that of a truncated cone or, when visualized as a molecular container, that of a cup (see Scheme 8). The binding constants of CDs range typically from 10 to 10^5 M^{-1},[227−229] which calls for millimolar macrocycle concentrations in order to achieve significant complexation of a fluorescent dye in aqueous solution. The derivative which is sufficiently large to firmly and deeply encapsulate a variety of organic residues such as aryl groups, but also more spherical and space-filling ones such as adamantyl, is the medium-sized β-CD;[228] it is unfortunately also the least water-soluble derivative (16 mM).[230] The smaller and larger homologues, α-CD and γ-CD, while more water-soluble (*ca.* 150 and 180 mM, respectively),[231] have a too small or too large cavity to ensure strong binding. In most cases, the complexation stoichiometry is 1:1, but there may be occasionally interferences from the formation of 2:1 and 2:2 guest/host complexes.[232−237]

To achieve deeper hydrophobic cavities, or higher water-solubility for dye binding, or to improve guest binding *via* enhanced ionic, ion-dipole, as well hydrophobic interactions (see Table 2), alkylated cyclodextrins (Scheme 7), such as HP-α-CD, HP-β-CD, Me-β-CD, Bu-β-CD, and HP-γ-CD as well as mono-BzSe-β-CD, mono-HP-β-CD, and mono-Et-β-CD, have been frequently used and studied with respect to their affinity for fluorescent dyes.[3,238−242] For β-CD, there are also several examples involving randomly or monosubstituted derivatives with charged groups (CM-β-CD,[170,243] SBE-β-CD,[169,244] mono-NH_2-β-CD[245]) or uncharged hydrophilic groups (mono-maltosyl-β-CD,[246] mono-glucosyl-β-CD,[242] and SHP-β-CD[247]). Another CD, which has recently been investigated for its fluorescent dye binding properties, is NH_2-γ-CD.[248]

3.2. Calix[*n*]arenes

The second most intensively investigated group of macrocycle-fluorescent dye complexes are those involving calixarenes (CX*n*). The calixarene skeleton is built up by base-catalyzed condensation of 4-substituted phenols with formaldehyde.[249] As a rule, the electron-rich hydroxyl- or alkoxyl-substituted aryl

Table 2. Photophysical Properties of Host/Guest Complexes

dye	host	K_{ass}/M^{-1}	I_{bound}/I_{free} [b]	λ_{ex} ($\lambda_{max,f}$) [a]/nm	conditions	ref
			Acridine Dyes (Scheme 1)			
PF	CB7	2.0×10^7	~2.8	400 (485)	phosphate buffer or H_2O	303
	CB8	1.9×10^7	~0.05	400 (509)	phosphate buffer or H_2O	303
AO	CB7	2.0×10^5	3	465 (514)	pH 7.0	50
		5.6×10^5	~5	485 (520)	PBS buffer (pH 7.5)	69
	β-CD	1.2×10^3	~0.75	455 (548)	pH 12.0	50
AY	CB7	$K_1 = 1.3 \times 10^4$	~6	440 (480)		161
		$K_2 = 1.2 \times 10^6$				
			Xanthene Dyes (Fluorenes) (Scheme 1)			
AR	β-CD	2.6×10^3	4	490 (553)	phosphate buffer (pH 7.2)	246
	mono-maltosyl-β-CD	1.8×10^3	3.6	490 (556)		
	mono-HP- β-CD	2.4×10^3	4.2	490 (553)		
	mono-BzSe-β-CD	8.0×10^3	~3	493 (555)	citrate buffer (pH 6.0)	242
	mono-glucosyl-β-CD	1.5×10^3	~2	493 (555)		
	C6SOc	4.3×10^4	~4	493 (564)		
	CX6	9.5×10^3	~0.33	493 (560)	citrate buffer (pH 6.0)	305
	C6SBu	2.3×10^4	~3.2	493 (560)		
PY	CB7	1.4×10^7	~1	~510 (−)	pH 5.5	67
	CB8	$3.2 \times 10^{13}\ M^{-2}$	~1	~510 (−)		
PYY	CB7	4.6×10^6	~1.8	556 (−)	pH 5.5	67
	β-CD	3.9×10^2	~0.5	515 (570)		58
	γ-CD	$78\ M^{-2}$	~0.6	515 (~562)		381
PYB	CB7	9.1×10^{6c}	~1.9	556 (571)		71
	β-CD	2.0×10^3	~0.5	515 (570)		58
	γ-CD	$42\ M^{-2}$	~0.6	515 (~570)		381
RhB	CB7	1.6×10^5	1.6	555 (582)		382
	β-CD	5.1×10^3	0.7	520 (573)	phosphate buffer (pH 7.2)	246
	mono-maltosyl-β-CD	3.3×10^3	0.8	520 (573)		
	mono-HP-β-CD	3.8×10^3	0.7	520 (572)		
	CX4	2.0×10^3	~0.8	400 (581)	phosphate buffer (pH 6.6)	306
	CX6	7.7×10^3	~0.4			
	CX8	1.4×10^5	~0.2			
	CB7	5.1×10^3	~2	520 (~575)	citrate buffer (pH 6.0)	383
	β-CD	5.9×10^3	~0.7			
	CX4	1.1×10^3	~0.7			
R123	CB7	$\sim 10^3$	~0.4	503 (532)		71
TMR	CB7	1.4×10^4	~1.3	559 (582)		71
KRS	CB7	$3-4 \times 10^5$	~2	567 (588)		167
RhBBE	CB7	1.1×10^5	4.7	555 (583)		382
R6G	β-CD [d]		~7	475 (593−604)		308
			~2	527 (561)		384
	CB7	1.2×10^{6c}	~1	527 (552)		287
Rh800	CX6	1.1×10^5	~0.6	610 (710)	PBS buffer (pH 7.2)	385
	CX8	4.6×10^5	~0.3	610 (710)		
BRB	β-CD	3.5×10^2	~0.7	556 (584)	pH 3.2	307
	HP-β-CD	2.9×10^2	~0.8			
	CX4	2.3×10^3	~0.7	490 (599)	tris-HCl buffer (pH 8.0)	386
	CX6	3.4×10^4	~0.5			
	CX8	4.8×10^4	~0.5			
			Xanthene Dyes (Fluorones) (Scheme 1)			
FS	β-CD		~1.5	450 (535)		308
	SQAM	4.7×10^4	~0.05	490 (~520)	MeOH/H_2O 9:1	282

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Table 2. Continued

dye	host	K_{ass}/M^{-1}	I_{bound}/I_{free} [b]	λ_{ex} ($\lambda_{max,f}$) [a]/nm	conditions	ref
TCTIF	β-CD		~1	546 (563)	pH 7.6	307
	HP-β-CD	2.4×10^2	~1.2	546 (564)		
	HP-γ-CD	1.4×10^2	~2	550 (~570)		387
ES	β-CD		~1	520 (550)	pH 5.0	307
	HP-β-CD	3.4×10^2	~1.2	520 (549)		
SAF	β-CD	1.1×10^3	~1.3	486 (511)	pH 3.2	307
	HP-β-CD	1.2×10^4	~1.5	486 (510)		
TCF	β-CD		~1	538 (562)	pH 7.6	307
	HP-β-CD		~1			
		Quinone-imine Dyes (Azines) (Scheme 2)				
NR	CB7	6.5×10^3	~8	450 (600)	pH 11.0	309
		6.0×10^5	~8	520 (600)	pH 2.0	
	CB8	$1.8 \times 10^{11}\ M^{-2}$	~0.1	509 (635)	pH 5.0	310
	β-CD	$K_1 = 4.1 \times 10^2$	~5	444 (588)	pH 9.0	75
		$K_2 = 4.2 \times 10^2$				
	HP-β-CD	1.0×10^3	~23	460 (575)	phosphate buffer (pH 7.5)	169
	SBE-β-CD	2.3×10^3	~31	460 (573)		
	CX4 [e]	3.5×10^3	~2	520 (620)	acetate buffer (pH 4.5)	311
	CX6 [e]	3.2×10^4	~2	520 (621)		
	CX8 [e]	3.1×10^6	~2	520 (618)		
ST	β-CD	1.6×10^2	~2.5	525 (573)	pH 7.2	170
	CM-β-CD	6.0×10^2	~3.1	527 (571)		
		Quinone-imine Dyes (Oxazines) (Scheme 2)				
NiB	tuR4A	7.5×10^5	~0.04	505 (579)	CH_2Cl_2	279
		9.8×10^6	~0.03	490 (544)	toluene	
NiR	β-CD	10	6.5	550 (~650)		86
	γ-CD		1.7			
OX	CB7	1.2×10^7	~1	591 (−)	pH 5.5	67
	CB8	$7.3 \times 10^{14}\ M^{-2}$	~0.28	591 (−)	pH 5.5	
OX1	CX8	$K_1 = 5.5 \times 10^6$	~0.03	610 (680)	pH 6.5	171
		$K_2 = 4.4 \times 10^5$				
BCB	β-CD	5.2×10^2	~1.6	635 (672)		312
	Me-β-CD	6.3×10^2	~1.6			
	mono-HP- β-CD	8.5×10^2	~1.9			
	mono-HEt- β-CD	7.5×10^2	~1.8			
MDB	β-CD	1.0×10^3	~2	567 (~650)		173
	γ-CD	$1.0 \times 10^4\ M^{-2}$	~0.5			
		Quinone-imine Dyes (Thiazines) (Scheme 2)				
TH	β-CD	1.8×10^3	~2	595 (623)		174
AZA	β-CD	3.3×10^2	~3	630 (~660)		70, 95
MB	CB7	1.3×10^7	~4.3	665 (685)	pH 5.5	74, 67
	CB8	$1.1 \times 10^{16}\ M^{-2}$	~3			
	CX4	1.4×10^5	~0.2	640 (698)	pH 7.5	313
	CX6	6.6×10^5				
	β-CD	4.1×10^2	~1.3	664 (688)	pH 5.0	307
	HP-β-CD	3.3×10^2				
TB	β-CD	4.4×10^2	~3	595 (~630)		173
	γ-CD	$2.5 \times 10^3\ M^{-2}$	~0.8			
NMB	β-CD	1.6×10^3	5.1	594 (~650)		70
	γ-CD	87	0.5			
		Arylmethane Dyes (Scheme 2)				
BPA	β-CD	8.0×10^4	~23	276 (305)		316
AuO	α-CD	5.0×10^3	~1.5	365 (~500)		388

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Table 2. Continued

dye	host	K_{ass}/M^{-1}	I_{bound}/I_{free} [b]	λ_{ex} ($\lambda_{max,f}$) [a]/nm	conditions	ref
	CX6	1.2×10^4	~1.3	365 (~510)	pH 7.0	178
	C6SPe	1.5×10^4	~6			
			Azo Dyes (Scheme 2)			
DBO	CB7	4×10^5	~0.73	374 (427)		118, 321
	β-CD	1.1×10^3	<0.2	358 (431)		117
	CX4	1.2×10^3	~0.1	365 (~420)	pD 7.4 (D_2O)	319
		4.7×10^3	~0.1	365 (~420)	pD 2.4 (D_2O)	
DBO-Amine	CX4	2.3×10^4	~0.1	365 (450)	acetate buffer (pH 6.0)	320
			Coumarin Dyes (Scheme 3)			
C153	β-CD	54	3.7	450 (550)		180
	γ-CD		2.1	405 (530)		322
7MC	β-CD	1.3×10^2	0.4	320 (395)		181
	HP-β-CD	1.2×10^2	0.4			
	γ-CD	41	0.75			
	HP-γ-CD	42	0.6			
Cou-6	β-CD		~10	445 (~505)		324
6MeC	CB8	$K_1 = 1.3 \times 10^4$	~5	320 (440)		183, 184
		$K_2 = 2.0 \times 10^6$				
4PBTC	CB7	1.4×10^4	~45	350 (410)	pH 3.5	389
HCD-1	β-CD	7.0×10^2	~6	344 (428)	pH 5.4	185
HCD-2	β-CD	3.4×10^2	~10	316 (434)		
HCD-3	β-CD	81	~2	302 (349)		
OST	β-CD	1.2×10^2	~2.6	340 (~400)		323
			Alkaloid Dyes (Scheme 3)			
PLM	CB7	4.3×10^4	8.2	347 (497)	phosphate buffer (pH 7.2)	325
DHC		7.9×10^3	5.8	350 (476)		
BE	CB7	1.6×10^6	500	400 (508)		329
		2.1×10^6	>100	345 (498)	pH 2.0	390
	CX4	3.0×10^3	~40	352 (546)	pH 2.0	328
	CX6	8.2×10^3	~13			
	CX8	$\sim 2.8 \times 10^5$	~40			
	β-CD	1.4×10^2	~10	348 (530)	phosphate buffer (pH 7.2)	330
CP	CB5	1.4×10^4	~60	357 (521)	Britton−Robinson buffer (pH 2.0)	331
	CB6	1.3×10^4	~45	357 (523)		
	CB7	1.9×10^4	~70	358 (520)		
	CB8	1.3×10^4	~30	359 (533)		
COR	CX4	$K_1 = 1.8 \times 10^7$	~0.4	372 (480)	1:2 complex, pH 2.0	334
		$K_2 = 6.1 \times 10^3$				
	CX8	6.5×10^5	~0.14	370 (520)	1:1 complex, pH 2.0	
SA	CB7	$K_1 = 1.4 \times 10^6$	~20	440 (558)	pH 4.0	333
		$K_2 = 1.0 \times 10^3$				
	CB5	1.2×10^4	~11	326 (541)	Britton−Robinson buffer (pH 2.0)	332
	CB6	6.7×10^3	~5	328 (552)		
	CB7	4.5×10^4	~20	326 (540)		
	CB8	1.2×10^4	~10	327 (548)		
			Miscellaneous (Polycyclic Aromatic Dyes) (Scheme 3)			
1,8-ANS	CB7	$K_1 = 19$	>100	370 (469)	phosphate buffer (pH 6.8)	335
		$K_2 = 1.6 \times 10^2$				
	α-CD	≤20	1.6	335 (~500)	phosphate buffer (pH 6.8)	3
	HP-α-CD	21	6.6			
	HP-β-CD	4.8×10^2	104			
	HP-γ-CD	2.4×10^2	17			
	β-CD	1.0×10^2	2.4	350 (510)	phosphate buffer (pH 7.2)	246
	mono-maltosyl-β-CD	69	2.1	350 (509)		
	mono-HP-β-CD	2.6×10^2	5.8	350 (499)		

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Table 2. Continued

dye	host	K_{ass}/M^{-1}	I_{bound}/I_{free} [b]	λ_{ex} ($\lambda_{max,f}$) [a]/nm	conditions	ref
2,6-ANS	CB6	52	~5	330 (~456)	0.2 M Na_2SO_4	284
	CB7	6.0×10^2	~25	370 (452)	phosphate buffer (pH 6.8)	335
	NH_2-γ-CD	1.7×10^4	17	318 (462)	acetate buffer (pH 5.5)	248
	α-CD	≤20	4.7	325 (~440)	phosphate buffer (pH 6.8)	3
	β-CD	1.4×10^3	31			
	HP-α-CD	1.1×10^2	36			
	HP-β-CD	7.2×10^3	82			
	HP-γ-CD	2.5×10^2	25			
2,6-TNS	β-CD	3.7×10^3	16	350 (483)	phosphate buffer (pH 7.2)	246
	mono-maltosyl-β-CD	2.4×10^3	28	350 (481)		
	mono-HP-β-CD	3.0×10^3	23	350 (480)		
	mono-NH_2-β-CD	$K_1 = 3 \times 10^3$	20	320 (~450)	phosphate buffer (pH 6.0)	245
		$K_2 = 72$				
PRODAN	β-CD	8.6×10^2	~10	360 (502)		247
	SHP-β-CD	1.4×10^3	~17	360 (494)		
R-BOH	α-CD	85	5.5	294 (355)		186
	β-CD	4.0×10^2	7.8			
S-BOH	α-CD	28	4.2	294 (355)		186
	β-CD	3.5×10^2	6.1			
AA	CB7	8.0×10^5	~3.7	342 (412)	pH 1.5	302
			~0.1	342 (512)		
PP	CX4	6.9×10^2	0.4	430 (580)	H_2O/MeOH 1:1 phosphate buffer (pH 8.0)	337
	CX6	5.8×10^3	0.1			
	tmR4A	2.3×10^5	0.5	430 (567)	0.01 M KOH/MeOH	336
	teR4A	4.2×10^6	0.7	430 (570)	phosphate buffer (pH 8.0)	338
	CyR4A	1.0×10^8	0.6			
HPTS	γ-CD	1.2×10^2	~6	405 (435)	pH 6.6	339
	AVCyc	4.7×10^4	~0.006	364 (512)	phosphate buffer (pH 7.4)	281
	AzaC4A	5.0×10^4	~0.16	390 (510)	HEPES buffer (pH 7.2)	255
	C4P	3.9×10^5	~0.08	440 (512)	pH 7.5	280
APB	β-CD	8.2×10^2	~3	328 (377)	pH 9.2	340
DANCh	CX8	3.3×10^5	~1.8	340 (558)	pH 6.9	188
DMN	α-CD	$8.2 \times 10^5\ M^{-2}$	~5	294 (361)	2:1 complex	341
	β-CD	1.3×10^3	~1	294 (361)	2:1 complex	
DEN	α-CD	$1.3 \times 10^4\ M^{-2}$	~28	294 (362)	2:1 complex	342
	β-CD	$2.7 \times 10^4\ M^{-2}$	~3	294 (362)	2:1 complex	
	γ-CD	$K_1 = 3.1 \times 10^2$	~0.7	290 (~390)	2:2 complex	391
		$K_2 = 6.7 \times 10^5$				
2NC	α-CD	$K_1 = 3.8 \times 10^2$	~0.5	295 (~365)		391
		$K_2 = 3.8 \times 10^2$				
	β-CD	1.7×10^3	~0.7	295 (370)		
23NC	γ-CD	$K_1 = 4.3 \times 10^2$	~0.6	309 (375)		391
		$K_2 = 3.2 \times 10^3$				
27NC	γ-CD	$K_1 = 6.0 \times 10^2$	~0.4	290 (~365)	2:2 complex	391
		$K_2 = 2.7 \times 10^6$				
HN12	α-CD	$6.9 \times 10^3\ M^{-2}$	~4.5	375 (475)	2:1 complex	187
	β-CD	7.0×10^2	~4			
	γ-CD	1.8×10^2	~4			
HAN	Me-β-CD	3.6×10^3	~4	365 (465)	phosphate buffer (pH 7.0)	343
		Miscellaneous (Polycyclic Heteroaromatic Dyes) (Scheme 3)				
ADZ	CB8		0.05	– (~408)		345
AADZ	CB8	$4.0 \times 10^9\ M^{-2}$	0.025	– (~508)		345
Me_2DAP	CB7	4.4×10^5	~1.5	338 (449)	phosphate buffer (pH 7.0)	347
	CB8	8.4×10^5	~1.7	338 (449)		346
DQ	CB7	3.5×10^2	~2	310 (365)	phosphate buffer (pH 7.0)	348
DPT	CB8	7.8×10^4	~7	360 (405)	phosphate buffer (pH 7.0)	349

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Table 2. Continued

dye	host	K_{ass}/M^{-1}	I_{bound}/I_{free} [b]	λ_{ex} ($\lambda_{max,f}$) [a]/nm	conditions	ref
LC	CB7	9.3×10^3	~1.8	350 (516)		350
	β-CD	9.7×10^2	~0.7	354 (~460)		351
QP	β-CD	2.2×10^3	~0.5	360 (~485)		193
ALP	β-CD	5.1×10^3	15	– (520)	(MeOH/H_2O 1:9)	352
KEP	β-CD	7.7×10^3	12	– (505)	(MeOH/H_2O 1:9)	352
CAP	β-CD	1.5×10^3	17	– (475)	pH 2.1 (MeOH/H_2O/1:9)	352
		7.5×10^3	0.2	– (419)	pH 9.2 (MeOH/H_2O 1:9)	
MBBI	CB8	5.7×10^5	~0.7	297 (341)	phosphate buffer (pH 7.0)	192
LCG	CX4	2.8×10^7	~0.007	460 (505)	water or phosphate buffer (pH 2.0–8.0)	354
	CX5	2.5×10^7	~0.007			
	CX4S	8.4×10^6	~0.007			
		Miscellaneous (Other Aromatic Dyes) (Schemes 4 and 5)				
Dapoxyl	CB7	2.0×10^4	200	336 (380)	pH 5.5 – 6.0	286, 320
	β-CD	5.5×10^3	7.8	353 (560)		137
DAPI	CB7	1.1×10^7	~12	361 (470)		355
DMABN	CB7		~10	282 (~475)		286
	α-CD	5.2×10^2	~4	304 (520)		207
	β-CD	5.6×10^2	~2.5	299 (535)		
TPP	CB8	1.5×10^5	~16	420 (590)	pH 1.0 (phosphorescence)	357
SQ	β-CD	$5.8 \times 10^5\ M^{-2}$	~4	560 (608)	pH 8.6	141
SQB	β-CD	2.7×10^3	~1.7	575 (636)	10% (v/v) EtOH/H_2O 2:1 complex	195
SQI	β-CD		~1.6	575 (640)	10% (v/v) EtOH/H_2O 2:1 complex	195
SQA1	β-CD	4.8×10^4	~6	600 (663)	10% (v/v) EtOH/H_2O 2:1 complex	195
SQA2	β-CD		~13	600 (666)	10% (v/v) EtOH/H_2O 2:1 complex	195
4-ASP	β-CD	1.0×10^3	5	440 (580)	$\lambda_{ex} = \lambda_{abs}^{max}$	359
	CX4	1.0×10^5	24	470 (570)	phosphate buffer/MeOH (pH 7.2)	358
	CX6	3.5×10^5	62	470 (574)		
	CX8	$K_1 = 3.0 \times 10^6$	7	470 (590)		
		$K_2 = 8.0 \times 10^5$				
2-ASP	β-CD	1.1×10^3	7.5	435 (552)	$\lambda_{ex} = \lambda_{max}^{abs}$	359
	β-CD	1.0×10^2	~4	440 (552)		197
MSP	CB7	1.0×10^6	5	396 (~510)		360
HPBI	CB7	2.4×10^6	~3	300 (437)	pH 4.0	214
		5.6×10^4	~1.8	302 (440)	pH 7.0	
HMPO	β-CD	1.4×10^3	~0.16	320 (400)		144
			~2	320 (465)		
LFLX	CX4	6.5×10^4	~0.3	292 (455)		362, 363
NFLX	CX4	8.1×10^3	~0.05	283 (452)	acetate buffer (pH 5.0)	361
	CX8	1.2×10^5	~0.1	280 (448)	Britton–Robinson buffer (pH 4.5)	392
2AF	β-CD	1.4×10^3	~3	320 (373)	pH 7.0	210
2AHF	β-CD	$K_1 = 5.3 \times 10^3$	~3	302 (370)	2:1 complex, pH 7.0	
ThT	CB5	$K_1 = 3.3 \times 10^5$	~5	390 (~499)		364
		$K_2 = 1.9 \times 10^3$				
	CB7	$K_1 = 1.2 \times 10^5$	~30	390 (~478)		
		$K_2 = 1.8 \times 10^3$				
	CB8 [f]	5.5×10^7	>100	390 (570)	excimer emission	297
	β-CD	$K_1 = 4.9 \times 10^3$	~1.3	330 (450)		365
		$K_2 = 4.0 \times 10^2$				
	γ-CD	$9.6 \times 10^2\ M^{-2}$	~25	440 (481)		
Aden	CB7	1.3×10^5	~0.2	276 (376)	pH 3.0	368
	β-CD	1.1×10^2	~2.5	290 (360)		367
Aden-1	CB7	4.2×10^4	~0.2	274 (390)	pH 3.0	368
Aden-2		3.6×10^4	~3.5	274 (388)		
BEA	CB6	2.7×10^4	~3.5	270 (292)		369
	CB7	1.0×10^4	~4			
	CB8	$9.5 \times 10^{11}\ M^{-2}$	~0.4			

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Table 2. Continued

dye	host	K_{ass}/M^{-1}	I_{bound}/I_{free} [b]	λ_{ex} ($\lambda_{max,f}$) [a]/nm	conditions	ref
ADBI	β-CD	2.1×10^3	~2	285 (310)		217
MBC	CB6	2.7×10^2	~10	285 (294)	0.2 M Na_2SO_4 (pH 7.6)	393
		$K_1 = 7.3 \times 10^4$	~1.6	298 (305)	acetate buffer (pH 4)	370
		$K_2 = 1.0 \times 10^6$				
	CB7	$K_1 = 6.6 \times 10^3$	~2	298 (305)	acetate buffer (pH 4)	370
		$K_2 = 7.5 \times 10^6$				
Cucurmin	CB6	$K_1 = 72$	~5	425 (520)	0.2 M Na_2SO_4	5
		$K_2 = 2.6 \times 10^2$				
	α-CD	$K_1 = 3.3 \times 10^3$	~2.1	425 (524)		238
		$K_2 = 5$				
	HP-α-CD	$K_1 = 1.2 \times 10^4$	~3	425 (520)		
		$K_2 = 28$				
	β-CD[g]	1.7×10^2	~3	425 (519)		
	HP-β-CD	$K_1 = 3.4 \times 10^3$	~6	425 (511)		
		$K_2 = 1.2 \times 10^2$				
	γ-CD[h,i]	$K_1 = 8.0 \times 10^3$	~3.5	425 (509)		
		$K_2 = 1.4 \times 10^2$				
	HP-γ-CD	$K_1 = 2.1 \times 10^4$	~0.25	425 (532)		
		$K_2 = 8$				
STIND1	β-CD	2.2×10^3	4.8	548 (586)	pH 7.2	371
	Me-β-CD	1.4×10^3	4.5			
STIND2	β-CD	7.6×10^2	1.3	514 (579)	pH 7.2	371
	Me-β-CD		1.1			
DHB	β-CD	2.6×10^2	3.5	517 (587)	pH 7.2	372
	Me-β-CD	1.4×10^2	3.4			
AP-Me	β-CD	1.2×10^2	5.4	376 (539)		373
AP-nPr		4.8×10^2	6.9	379 (535)		
AP-isBut		1.4×10^3	5.4	379 (540)		
AP-tBut		3.1×10^3	3.2	372 (540)		
AP-cHex		6.2×10^3	4.2	391 (543)		
NAP1	HP-β-CD	1.9×10^2	~3.5	430 (535)	phosphate buffer (pH 7.0)	394
	HP-γ-CD	1.1×10^2	~2.3	430 (543)		
NAP2	HP-β-CD	1.2×10^2	~1.8	430 (534)	phosphate buffer (pH 7.0)	394
	HP-γ-CD	3.0×10^2	~1.6	430 (541)		
NAP3	HP-β-CD	50	39	440 (524)	phosphate buffer (pH 7.0)	201
	HP-γ-CD	1.8×10^2	34	440 (528)		
MHN	β-CD	1.4×10^2	~0.4	– (395)		395
	γ-CD	60	~0.5	– (390)		
MBN	β-CD	5.5×10^2	~0.6	– (395)		395
	γ-CD	70	~0.3	– (389)		
NHN	β-CD	7.8×10^2	~0.6	260 (398)		395
	γ-CD	60	~0.5	260 (407)		
NBN	β-CD	2.0×10^3	~0.7	261 (403)		395
	γ-CD	2.6×10^2	~0.3	261 (383)		
DBN	α-CD[j]	$K_1 = 1.3 \times 10^3$	~20	320 (395)		202
		$K_2 = 3.3 \times 10^2$				
APP	Me_4CB6	6.8×10^5	~0.6	262 (424)	pH 2.6	276
HPI	CB6	$\sim 2.0 \times 10^4$	~8	249 (398)	pH 5.7	277
	Me_4CB6	$\sim 2.0 \times 10^4$	~250			
	CB7	$\sim 8.0 \times 10^4$	~0.05	249 (321)		
	CB8	$1.0 \times 10^{12}\ M^{-2}$	~0.1			
API	CB6	$\sim 8.0 \times 10^4$	>500	262 (424)	pH 5.7	277
	Me_4CB6	$\sim 2.0 \times 10^4$	>500			
	CB7	$\sim 8.0 \times 10^4$	~0.05			
	CB8	$8.0 \times 10^{11}\ M^{-2}$	~0.05	262 (365)		
DBF	β-CD	3.0×10^3	~2.1	316 (352)		208
	γ-CD [h]	$K_1 = 3.9 \times 10^2$	~1			
		$K_2 = 1.3 \times 10^4$				

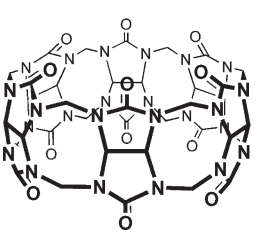
Table 2. Continued

dye	host	K_{ass}/M^{-1}	I_{bound}/I_{free} [b]	λ_{ex} ($\lambda_{max,f}$) [a]/nm	conditions	ref
DBFCA	β-CD	2.1×10^3	~0.6	286 (320)	pH 10.0	209
	γ-CD	4.5×10^2	~0.9			
DMAFP	β-CD	7.9×10^2	~6	446 (530)		211
DMAPNI	β-CD	$1.5 \times 10^4\ M^{-2}$	~4	340 (415)	1% MeOH (v/v)	203
DMAPIP	β-CD	4.1×10^2	~10	360 (424)	pH 9	204
		3.0×10^2	~6	385 (433)	pH 3.5	
AEC	CB6	2.2×10^7	~100	311 (375)	NH_4OAc buffer (pH 7.0)	212
			~0.1	311 (458)		
SNP	CB6	4.3×10^7	50	283 (334)	1 mM HCl (pH 3.0)	375
		2.5×10^3	>1000		acetate buffer (pH 5.5)	
DPOa	γ-CD	2.8×10^2	~0.6	300 (390)		233
DPOb		$6.1 \times 10^4\ M^{-2}$	~0.3	295 (390)	2:1 complex	
ABF	β-CD	5.7×10^2	~2.2	312 (373)		213
VK3	β-CD	1.4×10^2	~11	380 (410)	pH 7.6	244
	HP-β-CD	1.5×10^2	~28	380 (415)		
	SBE-β-CD	1.7×10^2	~35	380 (417)		
ADMP	β-CD	2.2×10^2	~2	288 (345)		215
QZ	α-CD	~80	~4	490 (570)		379
	β-CD	39	~9			
	γ-CD	96	~5.5			
DPABME	α-CD	45	~8	335 (510)		216
DAPS	β-CD	1.5×10^4	~24	296 (428)		380
	γ-CD	2.9×10^5	~13	290 (439)		396
3DAPS	β-CD	4.0×10^2	~4	290 (424)	pH 6.0	205
ANBT	β-CD	2.5×10^2	~5	350 (434)	pH 6.8 at 30 °C	218
H33258	CB7	1.7×10^6	~70	295 (470)	pH 7.2	220
		2.8×10^4	~11		pH 8.7	
		$K_1 = 1.5 \times 10^5$	~80	365 (480)	pH 7.0	397
		$K_2 = 1.0 \times 10^4$				
		$K_1 = 7.0 \times 10^5$	~3	353 (500)	pH 4.5	
		$K_2 = 9.0 \times 10^4$				
BISNAP	CB7	1.3×10^5	~35	360 (395)	pH 7.0	219
MAN	Et-β-CD	$3.0 \times 10^6\ M^{-2}$	~6	406 (505)	2:1 complex	398
RF	CB7	1.3×10^4	~0.6	460 (537)	pH 7.0	206
		6.7×10^3	~0.6	420 (532)	phosphate buffer (pH 7.0)	399
EPICO	α-CD	$K_1 = 1.4 \times 10^3$	~15	430 (542)		221
		$K_2 = 1.3 \times 10^2$				
	β-CD	$K_1 = 2.5 \times 10^3$	~3			
		$K_2 = 1.9 \times 10^2$				
PIC	CB7	2.1×10^4	~0.05	532 (581)	0.2 M NaCl at 10 °C	294
TO	CB8	$4.0 \times 10^{10}\ M^{-3}$	>500	488 (625)	2:2 complex	400
Cy5′	CB7	$\sim 10^4 - 10^5$	~1.7	642 (657)		71
3HBA	β-CD	6.2×10^2	~3	270 (365)	pH 1.0	401
		1.5×10^3	~0.6	260 (365)	pH 7.0	
		3.8×10^2	~2	280 (443)	pH 10.0	
AMBZ	β-CD	44	~6	– (335)	pH 1.1	222
		47	~1.3	– (370)	pH 6.9	
6ABT	β-CD	87	~2	318 (348)	pH 1.2	223
		68	~0.6	318 (420)	pH 6.9	
ADD	β-CD	1.9×10^2	~5.5	366 (440)	4% MeOH	224
4-ABP	CB6	5.0×10^5	30	360 (455)	NH_4OAc buffer (pH 7.0)	402

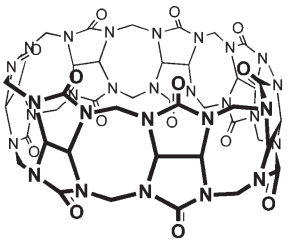
[a] λ_{ex} represents the fluorescence excitation wavelength. $\lambda_{max,f}$ represents the fluorescence maximum. [b] I_{bound}/I_{free} represents the relative fluorescence of the host/dye complex (I_{bound}) compared to the free dye (I_{free}). [c] See ref 382. [d] Concentration-dependent emission. [e] Initial increase, then decrease in fluorescence intensity. [f] Higher-order complexes are involved. [g] Data fit to 1:1 binding model. [h] Initial fluorescence quenching, then enhancement. [i] Did not fit 2:1 binding model exactly. [j] α-CD added to dye suspension in H_2O.

dx.doi.org/10.1021/cr200213s |Chem. Rev. 2011, 111, 7941–7980

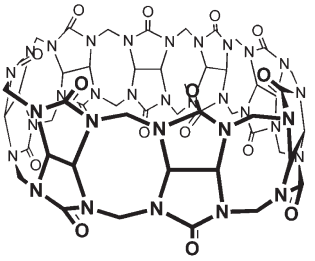
Scheme 6. Miscellaneous Macrocyclic Hosts[225]



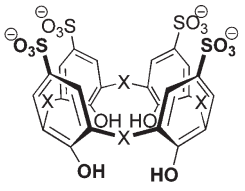
CB6



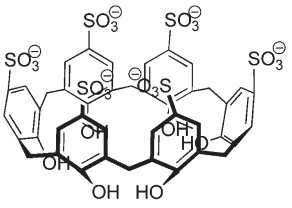
CB7



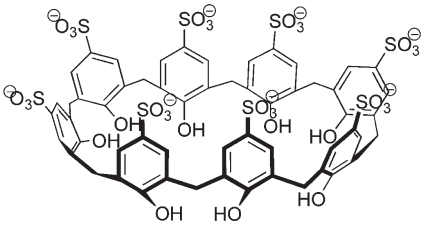
CB8



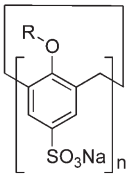
X = CH_2 (**CX4**)
X = S (**CX4S**)



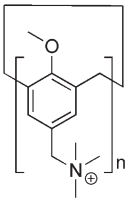
CX6



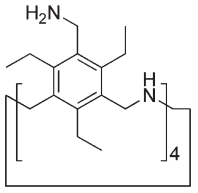
CX8



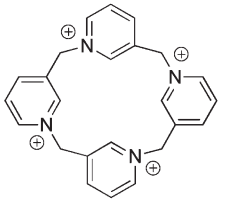
n = 5	R = H (**CX5**)
n = 6	R = C_4H_9 (**C6SBu**) R = C_5H_{11} (**C6SPe**) R = C_8H_{17} (**C6SOc**)
n = 8	R = $C_{10}H_{21}$ (**C8SDo**)



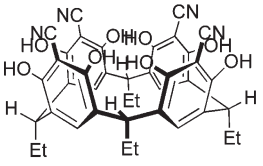
n	Name
6	**AC6**
8	**AC8**



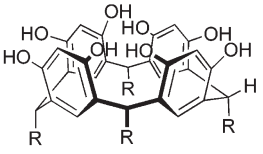
AzaC4A



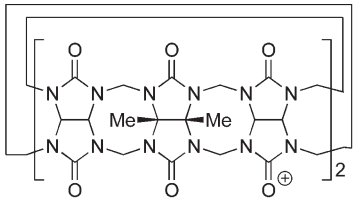
C4P



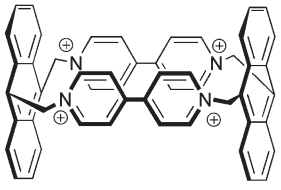
CyR4A



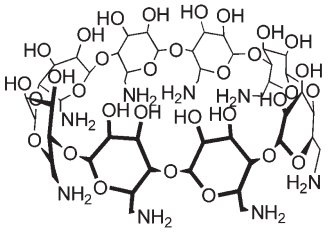
R = Me (**tmR4A**)
R = Et (**teR4A**)
R = $C_{11}H_{23}$ (**tuR4A**)



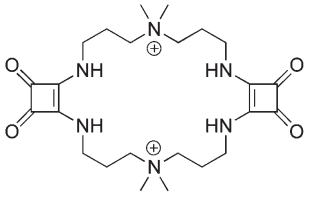
Me_4CB6



AVCyc



NH_2-γ-CD

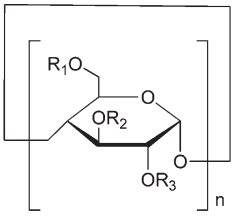


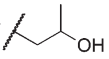
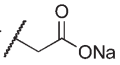
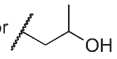
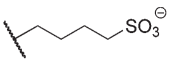
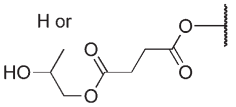
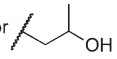
SQAM

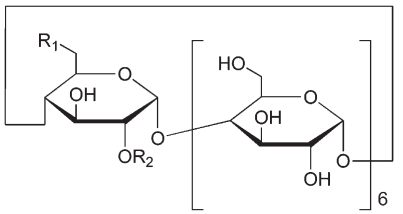
rings are prone to act as electron donors toward excited states, which leads to fluorescence quenching upon binding of fluorescent dyes. The sulfonated calixarenes introduced by Shinkai are the most prominent water-soluble homologues (Scheme 6).[250,251] They are commercially available in different sizes (CX4, CX6, and CX8), and the odd-numbered derivatives (e.g., CX5) can be synthesized as well.[252] While the smallest homologue, CX4, is also typically represented as a (flexible) truncated cone or cup (Scheme 8), the conformational variability of calixarenes is much larger than that of cyclodextrins. In particular, they can also adapt alternate conformations, e.g., CX6, which are then predestined for 2:1 guest/host binding. The conformational

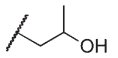
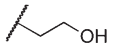
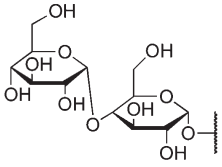
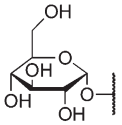
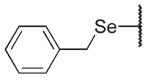
dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Scheme 7. Modified Cyclodextrins

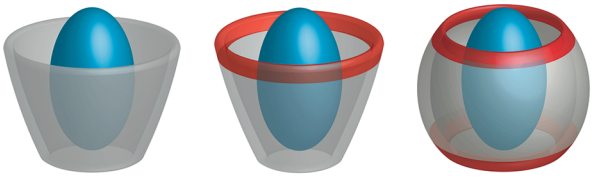


n	R_1	R_2	R_3	Compound
6	H	H	H	α-CD
	H or 			HP-α-CD
7	H	H	H	β-CD
	H or 			CM-β-CD
	H or 			HP-β-CD
	C_2H_5	H	C_2H_5	Et-β-CD
	CH_3	H	CH_3	Me-β-CD
	H or 			SBE-β-CD
	n-C_4H_9	H	*n*-C_4H_9	Bu-β-CD
	H or 			SHP-β-CD
8	H	H	H	γ-CD
	H or 			HP-γ-CD



R_1	R_2	Compound
OH		Mono-HP-β-CD
OH		Mono-HEt-β-CD
	H	Mono-Maltosyl-β-CD
NH_2	OH	Mono-NH_2-β-CD
	H	Mono-Glucosyl-β-CD
	H	Mono-BzSe-β-CD

Scheme 8. Representations of Inclusion Complexes for the Main Classes of Macrocyclic Hosts[a]



Cyclodextrin Calix[*n*]arene Cucurbit[*n*]uril

[a] Regions of negative charge density are shown as red rims.

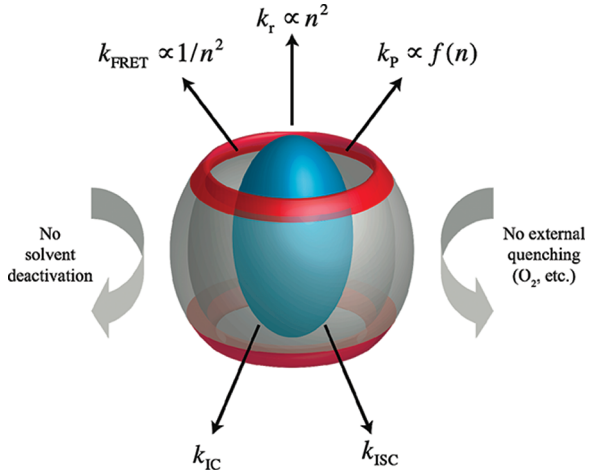
dynamics and variability can be greatly reduced by the alkylation of the phenolic hydroxyl groups (C6SPe, C6SBu, C6SOc, C6SDo). It should be noted that calixarenes, in particular the tetrameric ones, have a high preference for inclusion of spherical residues,[253,254] which matches the binding preferences of both cyclodextrins (*vide supra*) and cucurbiturils (*vide infra*). Most water-soluble functionalized calixarenes contain sulfonato groups; these constitute an upper rim with negative charge density (Scheme 8), which additionally accounts for their preferential binding with cationic guests. For fluorescent dyes, this preference presents rather an advantage than a limitation, because the majority of the popular dyes (see Schemes 1−3) are cationic in nature. However, several cationic calixarenes (Aza-C4A, AC6, and AC8) and a few water-soluble noncharged ones are available and have also been studied with respect to fluorescent dye binding.[255−257] Several of the calixarene derivatives with long alkyl chains display limited water-solubility; their amphiphilic nature, however, allows their refined use in micellized aqueous environments.[242,250,258−261]

3.3. Cucurbit[*n*]urils

Initially discovered by Behrend in 1905,[262] the third class of macrocycles, which are recently en vogue, are cucurbit[*n*]urils (CB*n*).[263] As for cyclodextrins and calixarenes, they occur in different sizes (Scheme 6): CB5, CB6, CB7, CB8, and CB10. The size of the inner cavity ranges from 68 to 691 Å^3 for CB5−CB10, allowing guest molecules of largely different sizes to be included within the cavity with remarkable selectivity.[264] Only recently, this class of macrocycles has been shown to exhibit low *in vivo* as well as *in vitro* toxicity, thereby facilitating biologically relevant applications.[265,266] They are obtained by acid-catalyzed condensation of glycoluril with formal-

dx.doi.org/10.1021/cr200213s |*Chem. Rev.* 2011, 111, 7941–7980

Scheme 9. Photophysical Decay Pathways for Excited-State Dyes upon Macrocyclic Inclusion



dehyde under carefully controlled conditions.[267−270] The even-numbered homologues display a low water-solubility, which is nevertheless sufficient to study their complexation with many fluorescent dyes, because the low solubility is counterbalanced by the fact that all cucurbiturils larger than CB5 can form much stronger host/guest complexes than cyclodextrins. Their binding constants range typically from 10^4 to 10^{15} M^{-1}, with exceedingly strong binding found in some cases.[271−273] Among the odd-numbered, water-soluble homologues, CB5 is too small to complex fluorescent dyes. However, CB7 displays a favorable combination of a sufficient cavity size and high water solubility (*ca.* 5 mM), which turns it into the most promising cucurbituril host for binding of fluorescent dyes. Substitution of the cucurbituril framework[273−275] is substantially more demanding than that of cyclodextrins and calixarenes, especially for the higher CB homologues, and there are only two case studies on the interaction of a substituted cucurbituril (Me_4CB6) with fluorescent dyes.[276,277] As is found to be the case with the sulfonated calixarenes, cucurbiturils act as cation receptors (due to their two identical carbonyl rim portals). This accounts for their high affinity toward most of the fluorescent dyes in Table 2. The tighter portals also impose a kinetic barrier on the complexation of organic guests, because their diameter is smaller than that at the equator.[278] This geometric feature also justifies the frequent pictorial representation of these molecular containers as a barrel (Scheme 8).

3.4. Other Macrocyclic Hosts

The binding of fluorescent dyes to other water-soluble macrocyclic compounds has been studied to a lesser extent. Structurally related to calixarenes are resorcinarenes. They possess a shallower cavity and lower water-solubility. The latter is frequently remedied by (partial) deprotonation of the phenolic hydroxyl groups, which requires the use of alkaline pH (for tmR4A) or the incorporation of electron-withdrawing substituents (for CyR4A). Derivatives with long alkyl chains (tuR4A) are no longer water-soluble.[279] Other macrocycles for which fluorescent dye complexes have been analyzed are the cyclophane AVCyc, the calixpyridine C4P, and the macrocyclic squaramide SQAM.[280−282]

Note that all macrocycles, and particularly cyclodextrins, cone/shaped calixarenes, as well as cucurbiturils, have a nonpolar (see below) inner cavity which is prone to bind organic residues or guests by hydrophobic interactions. The addition of charged substituents in cyclodextrins and calixarenes, e.g., aminated or sulfonated ones at one rim, respectively, allows a synergetic stabilization of the resulting host/dye complexes by electrostatic interactions. For cucurbiturils, the electrostatic stabilization is limited to ion−dipole interactions between the two carbonyl portals and the positively charged dyes (frequently as ammonium, iminium, or pyridinium salts). In general, calixarenes and cucurbiturils favor the binding of cationic guests over neutral ones,[264] while cyclodextrins have also an intrinsic affinity to anionic guests. Dispersion interactions become a sizable contributor for calixarenes, and they are important for dye binding, since most dyes contain polarizable aryl systems. The detailed interactions driving host/guest complexations and their binding mechanisms have been discussed in detail elsewhere.[264,283]

4. MACROCYCLE−DYE INTERACTIONS

The inclusion of chromophoric guests into the various macrocycles, most importantly fluorescent dyes, can affect their photophysical properties and potentially lead to unprecedented effects and, ultimately, new applications. Indeed, numerous studies have dealt with the changes of fluorescent properties upon complexation. We present a comparative compilation of selected host/guest systems where such effects have been documented in Table 2.

Let us first recall the different photophysical pathways which could be potentially altered by macrocyclic complexation, or confinement in general (Scheme 9). Upon excitation to the first singlet-excited state, several pathways of deactivation apply, including radiative decay (k_r), Förster resonance energy transfer (k_{FRET}), photoproduct formation (k_P), internal conversion (k_{IC}), intersystem crossing (k_{ISC}), solvent-induced quenching, and quenching by additives or oxygen. Details on these photophysical decay pathways are found in advanced textbooks.[30] The observed fluorescence effects upon host/guest complexation, either quenching or enhancement, can be traced back, in several cases, to predominant effects on the rate constant of a single process. In most cases, the effects of inclusion complexation are satisfactorily understood in terms of effects on k_{IC}, related to either (*i*) the relocation of the fluorophore into the more hydrophobic environment of the host cavities[3,8,284] or (*ii*) the geometrical confinement of the chromophore within the host, which restricts rotational and vibrational freedom,[71,285,286] thereby disfavoring nonradiative decay pathways. Additionally, upon complexation, the fluorophore might also be "mechanically" protected from external (intermolecular) quenchers, including the solvent and oxygen, by the walls of the macrocycle.[269,287] In particular, fluorescence quenching by oxygen can be suppressed, as observed, for example, for MB and DBO.[269,288] The solvent can interact with an excited dye, among others, by undergoing proton or hydrogen transfer reactions,[105,289−291] and it can promote single or multiphoton ionization processes,[291−293] all of which can ultimately lead to a permanent depletion of the chromophore by irreversible chemical follow-up reactions unless the ground states are efficiently recovered by conical intersections along the reaction pathway.[105,106,289−291,293] The latter is often the case for hydrogen atom abstraction processes[105,289,291]

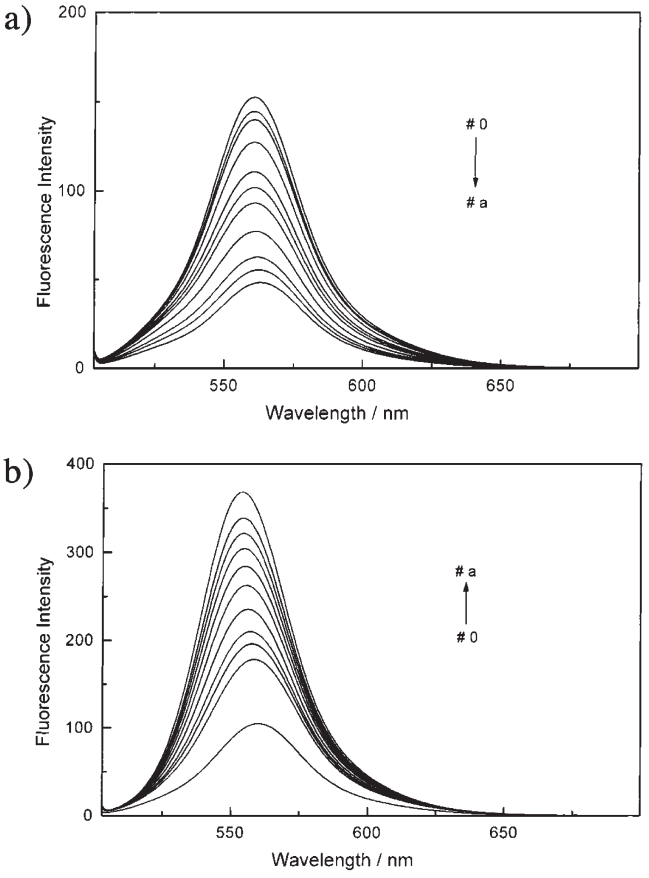


Figure 2. (a) Fluorescence spectra of AR (6.6×10^{-6} M) in the absence (top spectrum) and presence of up to 1.20 mM CX6 and (b) fluorescence spectra of AR (6.77×10^{-6} M) in the absence (bottom spectrum) and presence of (up to 427 μM) β-CD, all in aqueous citrate buffer solution (pH 6.00) at 25.0 °C. Adapted with permission from ref 305. Copyright 2000 American Chemical Society.

and those involving exciplex formation.[106] As a result of the encapsulation, dye aggregation may also be hindered, leading to notable changes in the photophysical properties of the dye-containing solution.[67,167,286,287,294−296] On the other hand, the formation of dimers may be promoted by hosts with larger cavities (e.g., CB8).[297] Furthermore, peripheral interactions (association rather than inclusion) between host and dye molecules can also lead to changes in fluorescence *via* host-mediated dye aggregates near the portals of the macrocycles.[298]

Besides photophysical effects on the fluorescent dyes caused by microenvironmental changes, confinement, and diffusional quenching, changes in chemical equilibria, particularly protonation equilibria, can also result in pronounced variations of their optical properties. For example, cucurbiturils cause large pK_a shifts in the ground[37,212,299,300] as well as the excited state;[214,301,302] the analysis of the resulting host-assisted guest protonation requires careful pH titrations and the application of the Förster cycle to comprehensively describe the effects of macrocyclic encapsulation.[27,28,30]

4.1. Acridine Dyes

Acridine dyes, such as acridine orange (AO) and proflavin (PF) bind to cyclodextrins (<10^4 M^{-1}) and particularly strongly to cucurbiturils (>10^5 M^{-1}), where they show additionally opposite fluorescence behavior for CB7 (enhancement) and CB8 (quenching).[50,303] The resulting inclusion complex of CB7 and AO

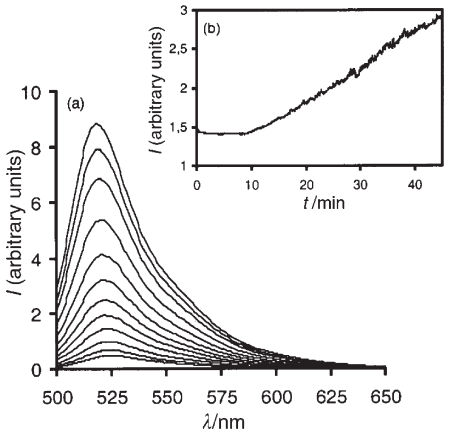


Figure 3. (a) Fluorescence quenching (λ_{exc} = 490 nm) of FS (1.4×10^{-5} M) upon addition of SQAM (up to 0.2 mM). The inset shows the response of the FS/SQAM ensemble to the constant addition of sulfate ions (from 0 to 200 ppm) over time. Adapted with permission from ref 282. Copyright 2001 Royal Society of Chemistry.

has also been investigated *via* computational methods, yielding valuable insights into the structural as well as photophysical characteristics of the complex.[304] Furthermore, deaggregation of AO upon its inclusion inside CB7 has also been investigated by ^{1}H NMR.[69] Acridine yellow (AY) forms 2:1 complexes with CB7, which is accompanied by a fluorescence enhancement.[161]

4.2. Xanthene Dyes

The xanthene dyes acridine red (AR), pyronine Y (PYY), and pyronine B (PYB) typically emit at *ca.* 560−580 nm. PYY and PYB show similar behavior upon host complexation: fluorescence enhancement inside CB7 and quenching inside β-CD.[58,67,71] The parent pyronine, PY, shows almost no change in fluorescence response upon inclusion inside cucurbiturils.[67] AR complexes (see Figure 2) have been studied with a number of modified cyclodextrins (fluorescence enhancement) as well as calixarenes (fluorescence quenching).[246,305] Futhermore, while its binding to cyclodextrins has been shown to be entropically driven, its complexation by calixarenes is the result of favorable enthalpic changes.[305] However, AR shows a fluorescence enhancement with a butyl sulfonatocalix[6]arene derivative (C6SBu), which has been attributed to the immersion of the dye between the hydrophobic butyl groups of the host.[305] The strongly emissive rhodamine dyes (RhB, R6G, and BRB) are generally quenched upon macrocyclic inclusion,[246,306,307] with the exception of R6G in β-CD, which leads to a fluorescence enhancement.[308] Due to their relatively large size, they bind more strongly to larger macrocycles such as CX8. However, the similarly sized and also highly emissive fluorescein-based dyes (SAF, ES, FS, TCF, and TCTIF) primarily show a small but distinct fluorescence enhancement upon complexation with cyclodextrins.[307,308] ES and TCTIF have been used to sense vitamin B6 *via* an indicator displacement approach (see section 7).[307] In an exceptional case, a remarkable quenching (95%) occurs for the complex between FS and a novel squaramide macrocycle, SQAM.[282] This host/dye system has been used to sense sulfate anions (see Figure 3) in solution *via* an indicator displacement approach (see section 7).

4.3. Quinone-imine Dyes

Quinone-imine dyes are subdivided into azines, oxazines, and thiazines. The azines neutral red (NR) and safranine T (ST) show a

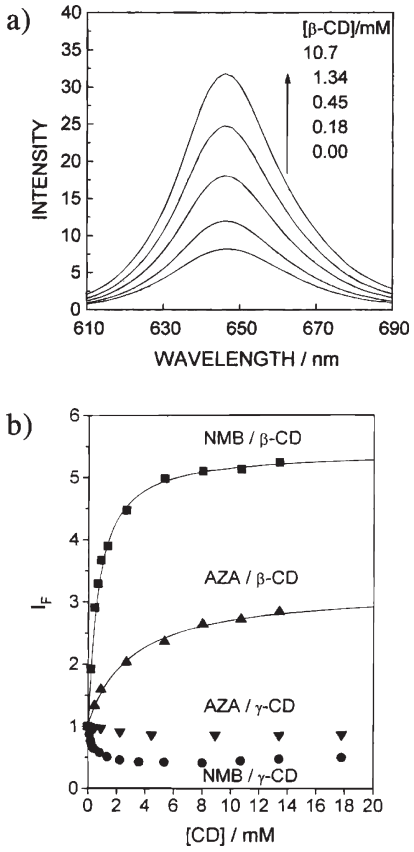


Figure 4. (a) Fluorescence spectra of 1.0×10^{-6} M NMB solutions at various concentrations of β-CD. (b) Plot of the fluorescence intensity against the concentration of different cyclodextrins (see legends) in 1.0×10^{-6} M NMB and AZA solutions. Adapted with permission from ref 70. Copyright 1999 American Chemical Society.

moderate binding with cyclodextrins and cucurbiturils, which is generally accompanied by an enhancement of fluorescence intensity.[75,170,309,310] NR, in particular, shows an impressive fluorescence enhancement with modified cyclodextrins (~30).[169] The fluorescence of NR is enhanced and quenched at low and high concentration of calixarenes, respectively.[311] The rotational dynamics of NR-CD complexes has also been investigated and shown to display a much longer relaxation time than that of the free dye.[75,309] ST has been shown to bind to DNA in either an intercalative (for the monomer) or electrostatic (for the dimer) manner.[170]

The encapsulation of oxazine dyes by various hosts has been investigated intensively as well. The strong complexation of nile blue (NiB) with a resorcinarene in organic media led to its fluorescence being strongly quenched.[279] Nile red (NiR), on the other hand, shows a fluorescence enhancement upon its (very weak) complexation by cyclodextrins.[86] Oxonine (OX) and oxazine (OX1) form strong 2:1 complexes with two similarly sized hosts, CB8 and CX8, and the fluorescence of both dyes is quenched upon encapsulation.[67,171] Brilliant cresyl blue (BCB) and Meldola's blue (MDB) form weak host/guest inclusion complexes with a range of cyclodextrin derivatives, which cause only a moderate increase in fluorescence intensity.[173,312]

Complexes of the thiazine dyes (TH, AZA, MB, TB, and NMB) have been studied with all hosts from Scheme 8. The complexation follows the general trends observed earlier, which are characteristic of the host molecules used. Cucurbiturils show a high binding affinity (MB) accompanied by a moderate fluorescence enhancement,[67] calixarenes quench the dye fluorescence (MB),[313] and cyclodextrins form weak complexes, which generally lead to a fluorescence enhancement of the dyes (TH, AZA, MB, TB, and NMB).[70,173,174,307] However, mild fluorescence quenching occurs (see Figure 4) with the larger γ-CD (AZA and NMB). Methylene blue (MB) presents an interesting case: albeit the dye does not show overwhelming changes in fluorescence intensity upon complexation, its relocation from the cavity of CX4 and CX6 to the cavity of CB7 would lead to a 20-fold fluorescence enhancement. This impressive fluorescence response could be potentially used in the design and analysis of multicomponent self-sorting systems.[314] In a recent application, MB/CB7 has been used to sense nicotine *via* the indicator displacement method.[315]

4.4. Arylmethane Dyes

The relatively hydrophobic arylmethane dye bisphenol A (BPA) shows a reasonably strong binding toward β-CD (8×10^3 M^{-1}), accompanied by a large fluorescence enhancement (23-fold).[316] ^{1}H NMR spectroscopy and semiempirical as well as DFT calculations have also been employed in the same study to give further insights into the structure of the BPA/β-CD complex. Another arylmethane dye, auramine O (AuO), shows strong binding and an increase in fluorescence intensity upon calixarene encapsulation.[178]

4.5. Azo Dyes

The bicyclic azo dyes DBO and DBO-Amine have been extensively studied and have a variety of applications in antioxidant sensing,[317,318] acetylcholine sensing,[319] and enzymatic assays.[320] These dyes have remarkably long fluorescence lifetimes (*ca.* 300 ns in water), which are dramatically enhanced (in the case of CB7) upon encapsulation (up to 1 μs).[100] Curiously, although the fluorescence lifetime increases in CB7, the fluorescence quantum yield slightly decreases upon inclusion (from 0.26 to 0.19 under deaerated conditions),[321] which can only be accounted for by assuming a decrease in radiative decay rate inside CB7.[71,118] This effect on the radiative decay rate has in fact been corroborated not only for DBO and its derivatives, but also for numerous other fluorescent dyes[71] and has its origin in the reduced polarizability of the cucurbituril cavity (see section 6). Note that the radiative decay rate increases with the square of the refractive index (which is directly related to the polarizability), such that microenvironmental effects can alter the fluorescent lifetimes and quantum yields in opposite directions.[321]

4.6. Coumarin Dyes

A large variety of coumarin dye complexes with cyclodextrins have been investigated by using fluorescence spectroscopy. These dyes form weak complexes with cyclodextrins (<1000 M^{-1}). While C153,[180,322] OST,[323] and the hydroxycoumarin derivatives, HCD-1, HCD-2, and HCD-3, all show a fluorescence enhancement upon encapsulation,[185] 7-methoxycoumarin (7MC) shows quenching.[181] Cou-6 has been shown to exhibit fluorescence enhancement upon binding to β-CD.[324] Other coumarins such as C460 and C480 have been used as probes to monitor solvation dynamics inside the γ-CD cavity.[225] Recently, the photodimerization of 6MeC within the CB8 cavity has been comprehensively investigated.[183,184] The guest fluorescence was enhanced up to 5-fold upon complexation, and interestingly, as a result of the geometrical deformation of the macrocycle (a case of an allosteric effect), the binding constant of the second guest

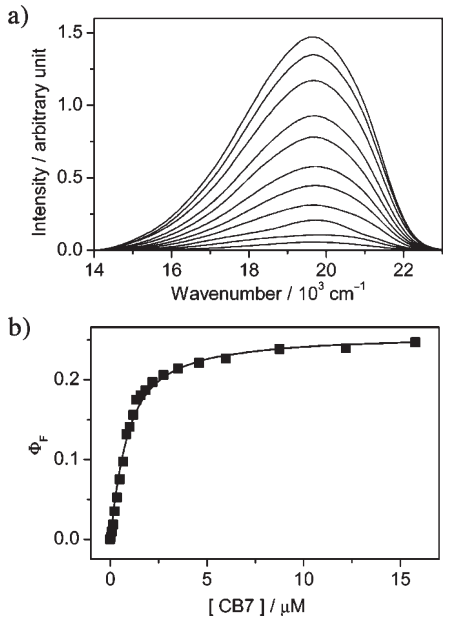


Figure 5. (a) Fluorescence changes upon addition of 0.079, 0.14, 0.23, 0.35, 0.50, 0.67, 0.84, 1.18, 2.19, 5.98, and 15.8 μM CB7 to 0.52 μM BE aqueous solution (λ_{ex} = 400 nm). (b) Fluorescence quantum yield of BE as a function of CB7 concentration. Adapted with permission from ref 329. Copyright 2008 American Chemical Society.

molecule to the 1:1 complex was found to be much higher than that of the 1:1 complex.

4.7. Alkaloid Dyes

The structurally related alkaloid derivatives PLM and DHC show a weak binding with CB7; however, a reasonable fluorescence enhancement upon inclusion has been demonstrated.[325] In a recent application, the PLM/CB7 dye/host pair has been used in indicator displacement assays to detect the presence of L-cystine and sotalol in aqueous solution.[326,327] The berberine alkaloid (BE) is a particularly interesting dye, because it shows fluorescence enhancement upon binding to all three of the common macrocyclic motifs, namely cucurbiturils, calixarenes, and cyclodextrins.[328−330] Furthermore, it has shown an exceptional fluorescence enhancement (*ca.* 500) upon its complexation by CB7 (see Figure 5).

Building on the striking fluorescence enhancement encountered upon the inclusion of BE inside CB7, coptisine (CP) and sanguinarine (SA) are other alkaloids that have more recently been investigated with cucurbit[*n*]uril homologues.[331−333] These two dyes bind moderately with the macrocycles and show fluorescence enhancements upon encapsulation. Consequently, the photo-oxidation as well as the nucleophilic attack at SA is inhibited by encapsulation inside CB7.[333] Furthermore, these effects have been successfully employed to sound out the presence of the alkaloid in human urine and serum samples. Coralyne (COR) shows a distinctly different behavior as compared to BE when included within calixarenes. First, its fluorescence is quenched upon encapsulation, and second, it forms 1:2 complexes with CX4 while maintaining a 1:1 complex with CX8.[334]

4.8. Polycyclic Aromatic Hydrocarbons

The widely used polarity-sensitive probes 1,8-ANS, 2,6-ANS, and 2,6-TNS generally show a weak binding affinity to a number

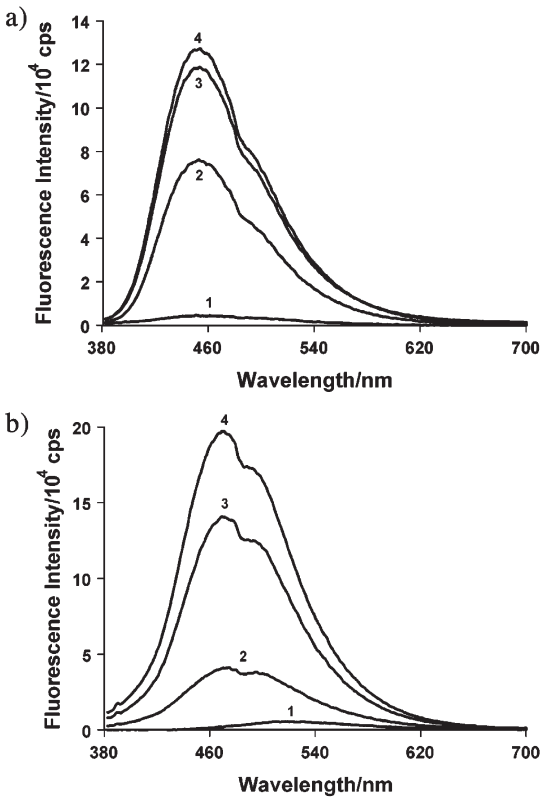


Figure 6. Fluorescence spectra of (a) 2,6-ANS and (b) 1,8-ANS in the presence of various amounts of CB7: (1) 0 mM; (2) 2 mM; (3) 6 mM; (4) 10 mM. Adapted with permission from ref 335. Copyright 2003 American Chemical Society.

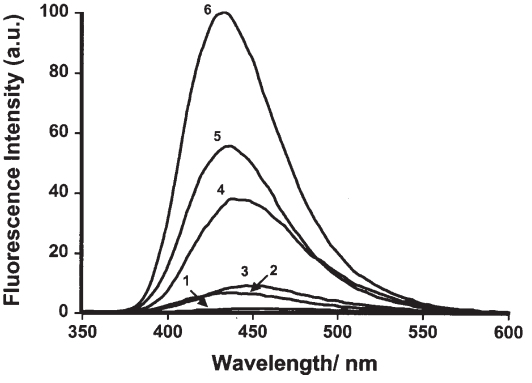


Figure 7. Relative fluorescence of 2,6-ANS in various cyclodextrin solutions (10 ± 1 mM in phosphate buffer): (1) no CD; (2) α-CD; (3) γ-CD; (4) β-CD; (5) HP-α-CD; (6) HP-β-CD. Adapted with permission from ref 3. Copyright 2000 Springer Science & Business Media.

of host molecules, accompanied by a marked fluorescence enhancement upon encapsulation, indicating the less polar interior of the hosts (see Figures 6 and 7).[3,245,246,257,284,335] Another polarity-sensitive dye, PRODAN, shows moderate binding with cyclodextrins with significant fluorescence enhancement.[247]

In order to investigate the chiral recognition properties of cyclodextrins, the binding of the binaphthol atropisomers R-BOH and S-BOH has been studied. However, no significant

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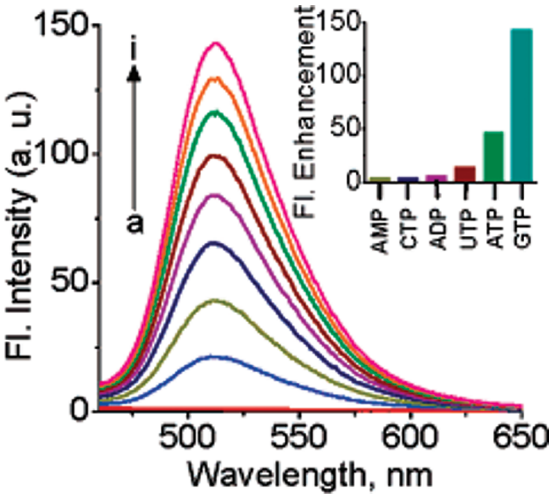


Figure 8. Fluorescence spectra of the HPTS/AVCyc complex upon the stepwise addition of GTP in phosphate buffer ([GTP] = 0−1.6 mM; a to i in the graph). The inset shows the relative fluorescence detection efficiency of various analytes at 1.6 mM by the HPTS/AVCyc system. Adapted with permission from ref 281. Copyright 2006 American Chemical Society.

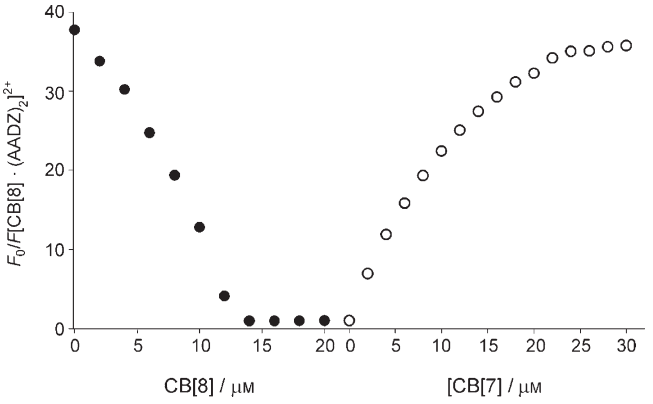


Figure 9. Fluorescence titration of AADZ (25 μM) with CB8 (●) followed by the addition of CB7 (○), which was monitored at 508 nm (pH 7). Adapted with permission from ref 345. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

difference is observed in the fluorescence or binding properties of the stereoisomers with α-CD or β-CD.[186]

Aminoanthracene (AA) binds quite strongly to CB7 in acidic media, and its fluorescence intensity is moderately enhanced.[302] The inclusion of AA inside CB7 shifts its excited-state pK_a value, thereby switching the fluorescence from its unbound neutral excited state (green emission) to that of the bound protonated excited state (blue emission).[302] The pyrene derivatives, PP, HPTS, and APB, have also been studied with a wide range of hosts. PP is quenched by calixarenes in a methanolic buffer and has been successfully used in combination with calixarenes to sound out the presence of acetylcholine in solution (see section 7).[336−338] HPTS binds strongly to the anthracene−viologen macrocycle, AVCyc, which has been attributed to the ionic interaction between the positively charged host (4 charges) and the negatively charged guest (3 charges).[281] The supramolecular interaction is accompanied by strong fluorescence quenching of HPTS (Figure 8). This system has been used to detect the presence of DNA nucleotides in solution, particularly GTP, through fluorescent indicator displacement.[281] As with AVCyc, a similar but less pronounced effect is observed in the case of complexation of HPTS with azacalixarene AzaC4A.[255] HPTS fluorescence is, however, enhanced within γ-CD. HPTS has been used to study excited-state proton transfer reactions within the cyclodextrin cavity.[339]

The APB/β-CD complex has been used as a saccharide sensor, which operated *via* a photoinduced electron transfer (PET) mechanism. In this regard, APB increases its fluorescence upon encapsulation and furthermore upon saccharide addition to the host/guest complex.[340] DANCh, a naphthalene-modified choline derivative, forms a strong complex with CX8 and has also been used as sensing system for acetylcholine.[188] Although the fluorescence response of the host/dye pair is not particularly high (factor of *ca.* 1.8), it is sufficient to detect the presence of the neurotransmitter in solution. Two structurally related naphthalene diester derivatives, DMN and DEN, form 1:2 (guest/host) complexes with α-CD, accompanied by a particularly impressive fluorescence enhancement in the case of DEN (factor of *ca.* 28).[341,342] The naphthol derivative, HAN, shows a moderate fluorescence enhancement when included inside cyclodextrins and has been used to probe confinement effects and dynamic processes in macrocyclic hosts as well as in proteins.[343,344]

4.9. Polycyclic Heteroaromatic Dyes

The binding characteristics of a number of polycyclic heteroaromatic dyes have been studied with cucurbiturils and calixarenes. Acridizinium (ADZ) and its amino derivative, AADZ, show a strong fluorescence quenching upon addition of CB8 (Figure 9).[345] However, upon subsequent addition of CB7, the AADZ fluorescence is recovered, thereby illustrating the switchable nature of these host/guest ensembles. The inclusion of 2,7-dimethyldiazapyrenium (Me_2DAP) inside CB7 and CB8 led to a moderate fluorescence enhancement regardless of the high binding constants.[346,347] Furthermore, the Me_2DAP/CB8 host/dye pair has been exploited as a sensor for catechol and dopamine *via* the formation of ternary complexes with each of these analytes, which could easily be monitored *via* the quenching of the fluorescence in the resulting ternary complexes.[346] The doubly charged DQ and DPT show a similar increase in fluorescence upon binding with CB7 and CB8, respectively. However, a very weak binding for the DQ/CB7 complex and, contrastingly, a strong binding for the DPT/CB8 complex were observed.[348,349] Intuitively, this contrasting effect can be attributed to the positions of the positively charged nitrogen atoms in each guest, thereby underlining the importance of the *spatial* optimization of electrostatic interactions between the host and the guest molecules, in this case, between the positively charged nitrogen atoms of the guest and the carbonyl portals of the cucurbituril host. Additionally, in a similar manner to the Me_2DAP/CB8 system, the DPT/CB8 dye/host pair was successfully used to sense indole derivatives such as serotonin and tryptophan.[349]

Lumichrome (LC) binds moderately to both β-CD as well as CB7 and shows an opposite fluorescence behavior upon encapsulation in each host (enhancement in CB7 and quenching in β-CD).[350,351] Furthermore, CB7 has been found to even induce the tautomerization of LC into its isoalloxazine-type structure.[350] QP, a phenoxathiin derivative, displays a typical binding propensity toward β-CD, which is accompanied by a moderate

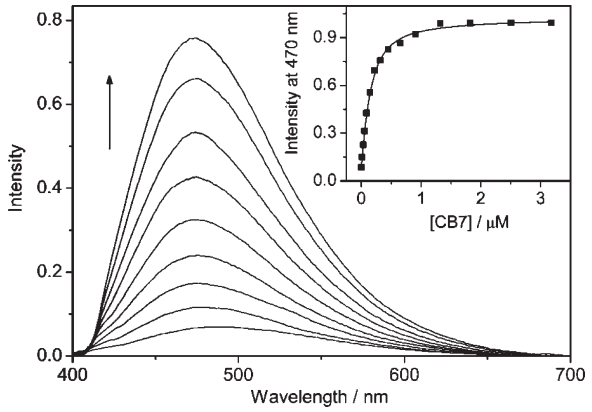


Figure 10. Variation of the fluorescence of 0.115 μM DAPI in aqueous solution upon addition of CB7 (0−3.18 μM, λ_{ex} = 361 nm). Inset: CB7 concentration dependence of the fluorescence intensity at 470 nm. Adapted with permission from ref 355. Copyright 2009 American Chemical Society.

fluorescence quenching.[193] However, other phenoxathiin derivatives (ALP, KEP, CAP) exhibit quite impressive fluorescence enhancements when complexed by β-CD.[352] Interestingly though, while the fluorescence of the carboxylic acid form of CAP is enhanced by β-CD, the deprotonated carboxylate form binds to the host 5 times more strongly and its fluorescence intensity is quenched upon binding.

MBBI has recently been used in combination with CB8 to provide an alternative motif for the formation of ternary complexes with small, electron-rich moieties such as tryptophan, which can readily be probed *via* photophysical methods.[353] By itself, it binds quite strongly to CB8 and its fluorescence is mildly quenched upon inclusion.[192] Only recently, the relatively large lucigenin dye (LCG) has been shown to bind very strongly (up to 10^7 M^{-1}) to calixarenes. This is accompanied by a spectacular quantitative fluorescence quenching upon encapsulation.[354] Furthermore, this host/dye conjugate has been successfully used to measure simultaneously choline and acetylcholine concentrations in solution *via* an indicator displacement approach (see section 7).

4.10. Other Aromatic Dyes

Dapoxyl, a known fluorescent intramolecular charge transfer (ICT) dye, shows an enormous fluorescent enhancement (*ca.* 200 times) of its locally excited (LE) band upon encapsulation by CB7 due to host-assisted guest protonation. Interestingly, the charge transfer (CT) band is enhanced as well, presumably due to polarity effects as well as guest confinement. This is evident from the fact that β-CD only enhances the CT band of Dapoxyl while leaving its LE band unchanged. The same effect applies to DMABN, another ICT dye, whose CT band is significantly enhanced upon encapsulation by both CB7 as well as β-CD.[207,286] DAPI binds strongly to CB7, while also showing a significant fluorescence enhancement upon complexation (see Figure 10).[355] DAPI, along with some of the alkaloids mentioned in section 4.7, has also been used to study the encapsulation of ionic liquid cations within the CB7 cavity *via* spectrofluorimetry.[356]

The TPP dye binds strongly to CB8, and as a consequence its phosphorescence emission becomes observable. This is the result of the hindered conformational mobility of the 2- and 6-phenyl rings of the dye within CB8 as opposed to CB7.[357] Note that TPP itself shows measurable phosphorescence neither at room temperature in aqueous solutions nor in the presence of CB7. The squaraine dye SQ forms a 2:1 host/guest complex with β-CD and its fluorescence intensity consequently increases.[141]

Two styrylpyridinium dye derivatives, 4-ASP and 2-ASP, have been investigated along with their complexes with calixarenes and cyclodextrins.[358,359] While both derivatives display a fluorescence enhancement upon binding to cyclodextrins, 4-ASP is significantly quenched upon its strong complexation by calixarenes. The β-CD/2-ASP host/dye system has been used further to investigate the binding strengths of various alkylamines, alkylammonium ions, as well as alcohols in solution *via* competitive displacement assays monitored by fluorescence.[359] More recently, the styrylpyridinium dye, MSP, has been shown to bind quite strongly to CB7, and its fluorescence intensity is consequently enhanced.[360]

HMPO, a proton transfer dye, is complexed by β-CD, which is accompanied by a fluorescence increase.[144] The photophysical properties of the excited-state phototautomer of HMPO are sensitive to internal rotations around the C2−C1′ bond, and this effect has been used to probe different microenvironments such as micelles and proteins.[144] Norfloxacin (NFLX) and lomefloxacin (LFLX) are synthetic antibacterial drugs that form relatively strong complexes with CX4, which is signaled by a strong fluorescence quenching.[361] Furthermore, a method for the sensitive determination (with a ng/mL detection limit) of LFLX in pharmaceutical preparations has been developed.[362,363] In the case of the two aminofluorene dyes 2AF and 2AHF, their fluorescence response upon complexation by β-CD is nearly identical. However, their complexation modes are quite contrasting; 2AF forms a 1:1 complex and 2AHF forms a 2:1 host/guest complex.[210]

Thioflavin T (ThT) forms 2:1 host/guest complexes with cucurbiturils as well as cyclodextrins, and its fluorescence intensity increases in all cases, most prominently for CB7.[364−366] The interplay between the binding stoichiometries of ThT with CB7 (1:1 and 2:1) and CB8 (1:2 and 2:2) as well as ternary complex formation with metal ions may be of interest for applications in drug delivery.[146,297,364,366] The unusual claim of CB5 binding to ThT could possibly be due to CB7 impurities in the host sample, since both hosts are water-soluble and are purified on the basis of their differential solubility in water.[268,269] The inclusion of adenine (Aden) and two of its derivatives (Aden-1 and Aden-2) has been investigated, and they display a strong binding with CB7. Interestingly, while the fluorescence of Aden and Aden-1 is quenched, the fluorescence of Aden-2 is enhanced.[367,368]

The benzimidazole derivatives BEA and MBC have been shown to have enhanced fluorescence when included within cucurbiturils.[213,369] Regardless of the similar structure of their binding moiety (benzimidazole), BEA binds 2 orders of magnitude more strongly to CB6 than MBC. BEA additionally forms a 1:2 host/guest complex with CB8, in which its fluorescence gets quenched. A highly sensitive assay for the detection of MBC (down to nanomolar concentrations), a common fungicide used on oranges, has also been developed.[370] ADBI, another benzimidazole derivative, binds moderately to β-CD along with a slight increase in its fluorescence intensity.[217]

The fluorescence of Cucurmin, the main ingredient of the turmeric spice, is extremely sensitive to the polarity of its environment. Its complexes have been investigated for a large variety of cyclodextrin derivatives.[5,238] The formation of mainly 2:1 host/guest complexes is observed, and their fluorescence increases upon inclusion, with the exception of HP-γ-CD, where quenching occurs. The two 2-styrylindolium dyes STIND1 and STIND2

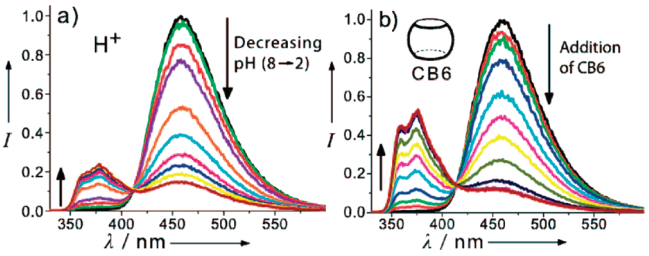


Figure 11. Fluorescence titrations of AEC (47 μM, λ_{ex} = 311 nm) (a) upon lowering the pH in water and (b) upon successive addition of CB6 (up to 50 μM) in 10 mM NH_4OAc buffer, pH 7. Adapted with permission from ref 212. Copyright 2008 American Chemical Society.

and the 2-styrylbenzothiazolium dye DHB show a moderate to weak binding toward cyclodextrins, which is accompanied by moderate fluorescence enhancements upon inclusion.[371,372]

β-CD complexes of a number of alkyl-substituted aminophthalimide derivatives have been investigated, and it has been shown that the binding strength of these complexes strongly depends on the size of the alkyl substituent.[373] Encapsulation is accompanied by moderate fluorescence enhancement of the respective dyes. Phenylazole derivatives, APP, HPI and API, show a strong binding with cucurbiturils, owing to their nitrogen-rich azole moieties, which strongly interact with the carbonyl portals of the macrocycles, while the hydrophobic phenyl group undergoes favorable van der Waals interactions with the interior cavity of the host.[276,277] The peculiar case here is that while HPI and API fluorescence is quenched within the larger cucurbituril homologues (CB7 and CB8), there is an astounding increase in fluorescence intensity (up to *ca.* 500 times) when they are encapsulated within CB6 and its tetramethylated derivative, Me_4CB6.[277] Curiously though, APP is quenched within the cavity of Me_4CB6.[276]

The dibenzofuran derivatives DBF and DBFCA, differing only in one functional group (alcohol versus acid), show an interesting opposite fluorescence response upon their moderately strong binding to β-CD.[208,209] While DBF exhibits a fluorescence enhancement, DBFCA is quenched upon inclusion. DMAFP, an intramolecular charge transfer dye and chalcone derivative, which is sensitive to the polarity of its microenvironment, is weakly bound inside the β-CD cavity, leading to an increase in fluorescence intensity of the dye.[211] DMFAP was further used to determine critical micelle concentrations as well as the polarity of the micellar core of several surfactants.[211]

AEC, a carbazole-based dye, has been specifically designed with a putrescine anchor group (see also section 5 on fluorescent tags) that would bind strongly to CB6.[212] The novelty of this design is that, upon binding, the amino groups of the anchor tend to be protonated, owing to host-assisted guest protonation,[374] thereby *blocking* the aromatic nitrogen atom from participating in charge-transfer. Furthermore, while the charge-transfer fluorescence band decreases, the locally excited band of the chromophore is enhanced (see Figure 11), thus enabling ratiometric fluorescence sensing with this reporter pair. The same principle has been implemented with the SNP/CB6 pair, for which a greater than 1000-fold enhancement of the fluorescence of the locally excited state was observed upon dye complexation.[375,376] In a related manner, the fluorescence of BISNAP is switched *via* blocking of photoinduced electron transfer upon complexation of the benzimidazole electron donor by CB7.[219] This concept has been used for the implementation of molecular logic gate operations.

The diphenyloxazole derivatives DPOa and DPOb can be encapsulated by γ-CD.[233] DPOa forms a 1:2 host/guest complex with this macrocycle, whereas, at higher host concentrations, DPOb forms 2:1 complexes. In both cases, however, fluorescence quenching is observed. ABF has been studied, and its complex with β-CD has been shown to display an excited-state pK_a shift of the amino group.[213] It binds weakly to the host and shows a moderate fluorescence enhancement. Vitamin K_3 (VK3), a naphthoquinone compound essential for blood coagulation, has been studied with a range of cyclodextrins.[244] While binding quite weakly to the hosts, it shows very large fluorescence enhancements upon complexation.

ADMP, a pyrimidine derivative, also showed a weak binding to β-CD but increased its fluorescence intensity upon encapsulation.[215] Quinizarin, QZ, has been studied with the parent cyclodextrin homologues as it undergoes both intra- as well as intermolecular hydrogen bonding, which significantly affects its photophysical behavior.[377,378] Thus, although its binding affinities toward the macrocycles are extremely weak, the corresponding increase in fluorescence is quite significant.[379]

DAPS, an important antileprotic as well as antimalarial drug, forms a relatively strong complex with β-CD, which is also accompanied by a notable increase in fluorescence intensity.[380] In comparison, its structural isomer, 3DAPS, binds quite weakly to β-CD, and the inclusion complex only shows a moderate fluorescence enhancement.[205] ADD, a nonconjugated bichromophoric dye, has a low affinity to β-CD but exhibits a moderate fluorescence enhancement upon complexation.[224]

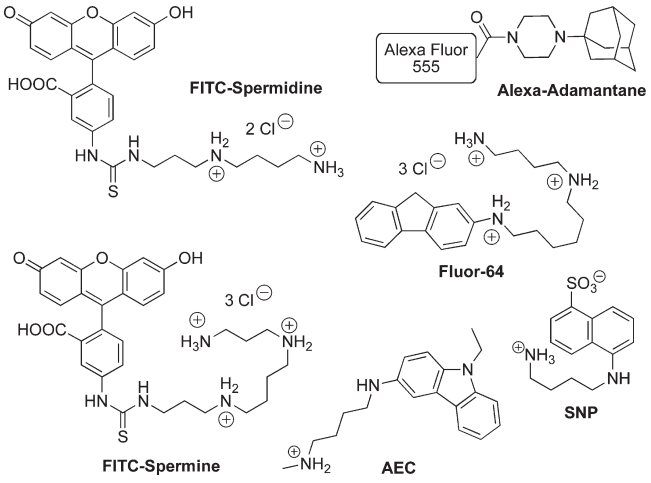
A wide spectrum of binding strengths (K_{ass}) coupled with varied fluorescence responses upon complexation provide a complete tool set of host/dye "reporter pairs" (see Table 2) for indicator displacement applications. Higher binding constants imply that these reporter pairs can be used in much smaller concentrations than those with moderate binding constants. Additionally, a large fluorescence response (I_{bound}/I_{free}) upon complexation, where a value greater than 1 indicates enhancement and a value less than 1 signals quenching, is highly desirable as this increases the sensitivity of the reporter pair.

5. FLUORESCENT TAGS FOR MACROCYCLIC HOSTS

The wide variety of host/guest complexes studied with the most commonly used macrocycles have provided a range of binding *motifs* that would be expected to almost certainly bind to the respective macrocycle with high affinity. For example, owing to their carbonyl-lined portals and hydrophobic interior cavity, cucurbit[*n*]urils (mainly CB6 and CB7) show remarkable binding propensities toward positively charged alkyl amines and polyamines, such as cadaverine, putrescine, spermidine, and spermine.[271,403−405] Furthermore, small, spherically symmetrical hydrophobic molecules, such as adamantyl derivatives, also show very high binding constants with CB7.[271,272] On the other hand, the phenyl backbone of calixarenes makes these hosts also suitable for binding aromatic moieties, due to favorable $\pi-\pi$ interactions, as well as for ammonium ions and their organic derivatives, owing to strong cation$-\pi$ interactions.[250,257,406−408] Cyclodextrins are, in comparison, quite unspecific in their preference for guest inclusion and show moderate binding to a variety of guest molecules.[228,409]

Using these well-known binding motifs as *anchor* groups, several fluorescent molecules can be covalently linked to them and the

Scheme 10. Fluorescent Tags for Cucurbiturils



resulting dye-anchor conjugates can be used as fluorescent tags in order to noncovalently *stain* and detect the presence of the respective macrocycles, regardless of whether the fluorescence response of the linked dye changes or remains the same upon complexation of the host with the anchor. As the anchor is encapsulated in the macrocycle, the fluorophore remains immersed in the bulk aqueous phase, which precludes conventional mechanisms of complexation-induced fluorescence changes, such as geometrical confinement or increased hydrophobicity. Hence, the fluorescence variations upon binding of the anchor are often small, which is desirable, for example, when the strong emission of near quantitative emitters needs to be retained. Exceptions are anchor dyes and macrocycles in which complexation is accompanied by a host-assisted protonation of amino groups, typically aryl amino groups, if they are integral components of the chromophore or act as quenchers[212,219] of the excited chromophore. In the former cases, protonation causes a switching from an intramolecular charge transfer state to a locally excited state (e.g., AEC and SNP);[212,375,376] in the latter case, the quenching pathway is shut down by deactivation of a redox-active nitrogen lone pair (e.g., BISNAP); see Table 2.[219] Noteworthy, the opposite effect, i.e., activation of photoinduced electron-transfer fluorescence quenching, has been observed for the peripheral complexation of a naphthalimide/amine conjugate by CX4.[410]

An early demonstration of the anchor concept involved the use of resorcinarenes, tmR4A and CyR4A, as macrocyclic hosts, *N*-methyl pyridinium as an anchor, and pyrene as appended dye.[336,338] The same dye/anchor conjugate (PP) binds in a similar fashion to CX6.[337] The *N*-methyl pyridinium anchor has also been utilized in another styrylpyridinium-based dye/anchor conjugate (4-ASP) and showed significant binding strengths toward CX4, CX6, and CX8 (see Table 2).[358] In all cases, complexation led to a change of the dye fluorescence, which, in turn, has been used to signal the presence of acetylcholine in solution *via* dye displacement from the host. This anchor moiety linked to a porphyrin has also been applied in combination with CB7 macrocycles to form higher order complexes.[411]

The binding of β-CD to a number of 4-amino-*N*-alkylphthalimide derivatives (see Scheme 4) has also been studied.[373] Their binding strength strongly depends on the nature of the alkyl substituents (e.g., adamantyl), which, effectively, behave as anchors to the cyclodextrin cavity. The fluorescence response of the dyes is enhanced upon complexation and has been applied to study the binding of surfactants to β-CD *via* a competitive displacement approach.

Probably one of the first fluorescent taglike molecules to be used in conjunction with cucurbiturils, namely CB6, was a fluorenyltriamine, Fluor-64 (Scheme 10), in the form of a fluorescence-switchable rotaxane.[412] Upon an increase in pH, the fluorenyl nitrogen is deprotonated, and consequently, the macrocycle relocates along the polyalkylamine chain from the hexyldiamine moiety toward the still diprotonated butyldiammonium segment. This switching affords both a fluorescence response as well as a color change. The fluorescein-derived FITC-spermine has been used as a tag to sound out the covalent linkage of CB6 to silica surfaces.[274,413] In a similar fashion, FITC-spermidine has been shown to efficiently tag CB6-based nanoparticles.[414] More recently though, both FITC-spermidine as well as Alexa-adamantane proved to be instrumental in biological studies with CB7 in cells.[265]

Table 3. Polarities of Macrocyclic Cavities Compared with Common Solvents and Solvent Mixtures as Determined with Solvatochromic Probes

probe	host	equivalent polarity	ref
1,8-ANS	β-CD	75% MeOH	239
	β-CD	55% EtOH	420
	HP-β-CD	EtOH	239
	Me-β-CD	EtOH	239
	CX6[a]	80% EtOH	420
2,6-TNS	α-CD	52% EtOH	257
	β-CD	59% EtOH	257
	CX6[a]	60% EtOH	257
	CX8[a]	85% EtOH	257
Pyr-CHO	β-CD	70% MeOH	415
	γ-CD	75% MeOH	415
DMABN	α-CD	*t*-BuOH	421
AP	β-CD	MeOH	422
2-NAP[b]	β-CD	alcoholic solvent	423
CNAP[c]	β-CD	1-PrOH	424
FN[d]	β-CD	alcoholic solvent	419
DPA	β-CD	EtOH	425
Pyr	CX8[a]	1-butanol	426
	β-CD	1-octanol	427
	γ-CD	1-octanol	427
Cucurmin	CB6	87% EtOH	5
R6G	CB7	1-octanol	287
DBO	β-CD	67% MeOH	117

[a] Modified macrocycles. See individualreferences. [b] 2-Naphthol. [c] 1-Cyanonaphthalene. [d] 9-Fluorenone.

6. APPLICATIONS OF SOLVATOCHROMIC PROBES

The fluorescence quantum yields of 1,8-ANS and 2,6-TNS increase characteristically in nonpolar environments. Pyrene and its derivatives (Pyr and Pyr-CHO), on the other hand, have been recognized to respond to polarity changes through the ratio of the 0−0 to 0−2 vibronic bands in the emission spectrum.[415] These well-known solvatochromic probes as well as some less common polarity-sensitive dyes (Table 2) have been used in combination

Table 4. Refractive Indices and Polarizabilities Inside Macrocyclic Host Molecules Determined by Using DBO and Biacetyl (Only for Hemicarcerand) as Solvatochromic Probes, Relative to Those in Solvents and the Gas Phase[118]

environment	polarizability (P)	refractive index (n)[a]
gas phase	0.000	1.000
cucurbit[7]uril	0.12	1.19
perfluorohexane	0.159	1.252
β-CD[b]	0.20	1.33
H_2O	0.206	1.333
n-hexane	0.229	1.375
CX4[c]	0.25	1.41
benzene	0.295	1.501
diiodomethane	0.404	1.742
hemicarcerand	0.45	1.86

[a] Refractive index, converted using the formula $P = (n^2 - 1)/(n^2 + 2)$. [b] See ref 321. [c] See ref 319.

with different macrocycles in an effort to assess microenvironmental effects of dye encapsulation and, by comparison with the photophysical properties in different solvents, to assess the polarity of the inner cavity of macrocyclic hosts.[5,245,246,257,287,335,354] All studies along this line have confirmed the entirely intuitive expectation that a dye immersed inside a macrocycle experiences an environment that is less polar than that of water, but at the same time does not reach that of nonpolar organic solvents, owing to the incomplete insulation from the aqueous bulk.

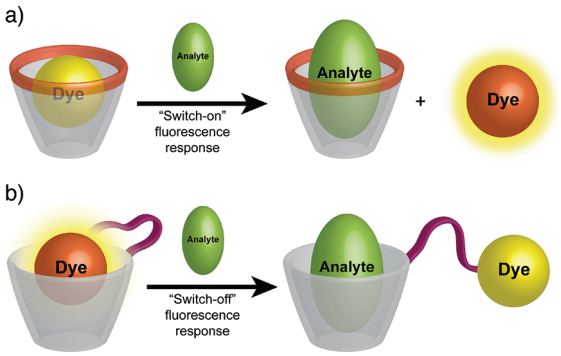
It should be noted here that the polarity of a medium and similarly that of a microenvironment is a difficult concept, since it presents a conglomerate of different unspecific as well as specific solute−solvent interactions, including hydrogen bonding.[30,416] In those cases where a direct comparison with solvents and solvent mixtures has nevertheless been attempted (Table 3), the apparent polarities generally resemble those of alcohols or water−alcohol mixtures for all investigated hosts, prominently cyclodextrins, selected calixarenes, and two cucurbituril homologues. The polarity extracted for one and the same host, e.g., β-CD, shows rather large variations in dependence on the selected probe, which exposes a limitation of the use of solvatochromic probes to explore macrocyclic cavities. One reason for the variation appears to be that different fluorescent dyes are immersed to different degrees and in different orientations inside the same macrocycle. For a solvatochromic probe to afford meaningful information on the polarity of the cavity, it would be required to be fully immersed, which is fulfilled only for the smallest probes. Second, different mechanisms are responsible for the fluorescence changes of dyes upon macrocyclic encapsulation (see Scheme 9 in section 4). Before applying a fluorescent dye as a solvatochromic probe for the polarity of the microenvironment, it is important to ensure that the fluorescence response is not related to another effect, for example, a classical confinement effect (see section 4) limiting either relaxation of the solvent[344,417,418] or internal rotation of the dye.[71,285,357,388] Besides the experimental studies aimed at quantification of the microenvironmental polarity, there are also several studies that have assessed the polarity of cyclodextrin cavities in a qualitative sense.[409,419]

The azoalkane DBO and the diketone biacetyl have been employed as *polarizability*-sensitive solvatochromic probes (Table 1), since their optical properties (oscillator strength of the n,π^* absorption band of DBO and phosphorescence emission maximum of biacetyl) depend on the polarizability (refractive index) of the environment.[118,321,428] These probes have the advantage of being sufficiently small to be fully immersed inside prototypal host cavities such as those of β-CD,[429−431] CX4,[319,432] or CB7.[118,286]

The studies on cavity polarizability have afforded an exceptionally low polarizability of the cavity of CB7 and an exceptionally high polarizability of the interior of a hemicarcerand, which provided support for an early hypothesis by Cram, namely that the inner phase of supramolecules could behave as a new phase of matter.[433] In contrast, the polarizability inside β-CD has been found to be similar to that of water and alcohols, in agreement with the cavity-polarity studies (*vide supra*).[321] The polarizability inside CX4 fell slightly below that of benzene.[319]

Knowledge of the polarizability of macrocyclic hosts is important for the understanding of the photophysical properties of immersed fluorescent dyes. In particular, their radiative decay rate increases with the square of the refractive index of the environment,[434] which is directly related to its polarizability (see footnote *a* in Table 4). This is the reason, for example, that the fluorescence lifetimes of numerous dyes immersed in CB7 (which has a low-polarizability environment) are longer than those measured in any other condensed phase.[71,287] The fluorescence lifetime of DBO immersed inside CB7 (1 μs) is the longest one known for an organic compound in aerated aqueous solution, in particular, and in a condensed phase, in general.[269,435]

Scheme 11. Indicator Displacement Assays for Analyte Sensing Using (a) an Intermolecular Macrocycle/Dye Reporter Pair and (b) an Intramolecularly Tethered Macrocycle/Dye Conjugate[a]



[a] A "switch-ON" and "switch-OFF" fluorescence response (schematically illustrated for a calixarene and cyclodextrin) are arbitrarily shown for the former and latter case.

7. ANALYTE SENSING BY FLUORESCENT DYE DISPLACEMENT

The complexation of a fluorescent dye by a macrocycle leads to readily detectable changes of its fluorescence properties, prominently its intensity (see section 4 and Table 2). Conversely, its decomplexation reverses these changes, and this process can also be accurately monitored. From a practical point of view, such decomplexation can be induced by the addition of an analyte, which can in this manner be indirectly detected by fluorescence

Table 5. Reporter Pairs Composed of Fluorescent Dyes and Macrocycles Utilized for the Detection of Analytes by Indicator Displacement Strategies

reporter pair					
dye	macrocycle	analyte[a]	solvent	fluorescence response[b]	ref
RhB	CX8	acetylcholine	phosphate buffer, pH 6.6	switch-ON	306
R6G	C8SDo	acetylcholine	phosphate buffer, DMPC, pH 6.9	switch-ON	462
Rh800	CX8	acetylcholine	phosphate buffer, pH 7.2	switch-ON	385
PP	tmR4A	acetylcholine	KOH/MeOH	switch-ON	336
PP	CyR4A	acetylcholine	phosphate buffer, pH 8.0	switch-ON	338
PP	CX6	acetylcholine	water/MeOH, pH 8.0	switch-ON	337
4-ASP	CX6	acetylcholine	phosphate buffer/MeOH, pH 7.2	switch-ON	358
2-ASP	β-CD	alkylamines/alkyl alcohols	phosphate buffer, pH 7.0	switch-OFF	359
2-ASP	β-CD	alkylammonium ions	0.1 N HCl	switch-OFF	359
DBO	CX4	acetylcholine	D_2O, pD 2.4/7.4	switch-ON	319
DANCh	CX8	acetylcholine	water, pH 6.9	switch-ON	188
HPTS	AVCyc	ATP	phosphate buffer, DMPC, pH 7.4	switch-ON	281
HPTS	AVCyc	nucleotides	phosphate/succinate buffer, pH 7.4/6.5	switch-ON	248
HPTS	AzaC4A	inositol triphosphate	HEPES buffer, pH 8.2	switch-ON	255
HPTS	C4P	ATP	water, pH 7.5	switch-ON	280
1,8-ANS	AC6	nucleotides	D_2O	switch-ON	256
1,8-ANS	AC8	nucleotides	D_2O	switch-ON	256
1,8-ANS	HP-β-CD	acetoxychavicol acetate	PBS buffer (pH 7.4) with 3% ethanol	switch-OFF	463
2,6-ANS	NH_2-γ-CD	nucleotides	acetate buffer, pH 5.5	switch-OFF	248
FS[c]	SQAM	SO_4^{2-}	water/MeOH	switch-ON	282
DBO	CX4	metal ions	D_2O, pD 2.4/7.4	switch-ON	455
DAPI	CB7	imidazolium	water	switch-OFF	355
BE	CX4	imidazolium	water, pH 2	switch-OFF	456
BE	CX6	imidazolium	water, pH 2	switch-OFF	456
BE	CB7	Na^+	water	switch-OFF	329
BE	Bu-β-CD	cetyltrimethyl-ammonium	water/membrane	switch-OFF	241
PLM	CB7	L-cystine	water	switch-OFF	326
PLM	CB7	sotalol	water	switch-OFF	327
NR	CB7	Na^+	water, pH 7.5	switch-OFF	309, 464
DBO-Amine	CX4	biogenic amines	acetate buffer, pH 6	switch-ON	320, 457
Dapoxyl	CB7	biogenic amines	acetate buffer, pH 6	switch-OFF	320, 457
DBO-Amine	CX4	arginine	H_2O, pH 9.5	switch-OFF	465
4-ABP	CB6	biogenic amines	acetate buffer, pH 7.0	switch-OFF	402, 466
LCG	CX4	acetylcholine/choline	phosphate buffer, pH 8.0	switch-ON	354
BISNAP	CB7	cadaverine	pH 7.0	switch-OFF	219
SNP	CB6	gaseous hydrocarbons	acetate buffer, pH 5.5	switch-OFF	375
MB	CB7	nicotine	water	switch-OFF	315
AO	CB7	cadaverine	ammonium phosphate, pH 7.2	switch-OFF	465
AO	CB7	insulin	phosphate buffer, pH 7.0	switch-OFF	467
AO	CB7	bis(cyclopentadienyl)cobalt(III)	phosphate-buffered saline, pH 7.5	switch-OFF	69

[a] Where several potential analytes have been studied, the one with the largest fluorescence response/binding constant is given. [b] Upon analyte binding. [c] Same structure as in Scheme 1, but as disodium salt.

of an "indicator dye" (see Scheme 11).[336] In fact, many of the host/dye pairs compiled in Table 2 have been studied with such applications in mind. The system of macrocycle and fluorescent dye sets up a "reporter pair" for the sensing of various analytes.[320] The nature of the macrocycle determines both the selectivity and sensitivity of this popular approach for analyte sensing.[436,437] Whether a fluorescence decrease (switch-OFF response) or increase (switch-ON) is observed upon analyte binding depends on the change of the fluorescence properties upon complexation; that is, a switch-ON response (which is frequently preferable) is observed in those cases in which the dye is quenched upon inclusion complex formation ($I_{bound}/I_{free} < 1$ in Table 2).

7.1. Detection and Quantification of Analytes

Covalently linked macrocycle/dye conjugates (intramolecular variant shown in Scheme 11b) have also been employed successfully

Table 6. Reporter Pairs Composed of Fluorescent Dyes and Macrocycles Utilized for Enzymatic Reaction Monitoring and the Direct Continuous Time-Resolved Detection of Substrates of Products, All in Aqueous Solution

reporter pair					
dye	macrocycle	enzyme	substrate/product[a]	fluorescence response[b]/assay-type	ref
DBO-Amine	CX4	amino acid decarboxylases	amino acids/biogenic amines	switch-ON/product-selective	320, 457
Dapoxyl	CB7	amino acid decarboxylases	amino acids/biogenic amines	switch-OFF/product-selective	320, 457
AO	CB7	thermolysin	polypeptides/dipeptides	switch-OFF/product-selective	468
AO	CB7	lysine decarboxylase	lysine/cadaverine	switch-OFF/product-selective	465
AEC	CB6	lysine decarboxylase	lysine/cadaverine	ratiometric/product-selective	212
DBO-Amine	CX4	arginase	arginine/ornithine	switch-OFF/substrate-selective	465
AO	CB7	diamine oxidase	cadaverine/5-aminopentanal	switch-ON/substrate-selective	465
2,6-ANS	NH_2-γ-CD	potato apyrase	nucleotide tri-/monophosphates	switch-ON/substrate-selective	248
LCG	CX4	choline oxidase	choline/betaine	switch-OFF/substrate-selective	354
HPTS	AVCyc	potato apyrase	nucleotide tri-/monophosphates	switch-OFF/substrate-selective	248

[a] Stronger competitor is underlined. [b] Upon enzymatic conversion.

for analyte sensing by indicator displacement.[10,438−450] Although not dealt with in detail in this review, but elsewhere,[451] it should be mentioned that these systems have their merits and disadvantages when compared to the intermolecularly assembled reporter pairs. Due to the proximity of the tethered macrocycle, a high local concentration is always ensured, thereby maximizing in an advantageous manner the abundance of the inclusion complex in the absence of analyte. Drawbacks are that they require a laborious synthesis and clever design, e.g., the tether must be sufficiently long and flexible, and that they offer less variability in the experimental setup than the intermolecular reporter pairs. The latter provide ready access to libraries of fluorescent dyes and additionally allow (to highlight a rarely emphasized benefit) the concentration of macrocycle to be adjusted in order to match the affinity range of a particular analyte. Note that a good rule for a convenient and sensitive indicator displacement assay is that the affinity product (defined as binding constant *times* concentration) should be about equal for the dye and the analyte.[354]

Reporter pairs, which have been employed for the sensing of different analytes, are compiled in Table 5. There are additional examples in organic solvents,[452,453] which are potentially transferable to the aqueous solution measurements covered by this Review. The classical example is the use of calixarene/dye reporter pairs for acetylcholine sensing. Even though the first system had been reported as early as 1994,[336] systems operational at neutral pH only followed later,[337] and fully water-soluble reporter pairs have emerged only recently.[188,306,319,338,354,358,454] Other popular examples are host/dye systems for nucleotide sensing, which compete with the more complex chemosensing constructs designed for the same purpose.[248,256,280,281] Finally, depending on whether the macrocycle acts as cation or anion receptor, simple ionic analytes have also been sensed by displacement of fluorescent dyes from macrocyclic complexes.[282,329,355,455,456] Dapoxyl, in combination with CB7, has been introduced to sense and quantify different amino acids in a multiparameter sensing array.[457] In a pattern-recognition approach, a combination of several host/dye reporter pairs collectively employed in a colorimetric sensor array has been used to discriminate between several structurally similar amines in solution[458] as well as biologically relevant metabolites.[459] Furthermore, these sensor arrays have been utilized to detect amino acids[460] and discriminate between them, as well as for the identification of quaternary ammonium salts.[461]

7.2. Time-Resolved Monitoring of Analyte Formation or Depletion

The displacement of the fluorescent dye from the reporter pair can be exploited not only to assess absolute concentrations of analytes but also to assess their relative changes with time. The latter has been employed in combination with enzymes, where the formation of a strongly binding product of an enzymatic reaction is monitored (product-selective assay).[212,320,457] This methodology (supramolecular tandem enzyme assays, Table 6) has been further exploited for the depletion of a strongly binding enzymatic substrate, in which case there is an uptake of the fluorescent dye in the course of the enzymatic reaction (substrate-selective assay).[465] The fluorescence response of the systems in the two cases is expectedly opposite and can again be switch-ON or switch-OFF.[320,465] Because this enzyme assay method requires, instead of specific recognition, merely a differential binding of substrate and product, it can be quite broadly applied to enzymatic reactions as well as to the detection and quantification of concentrations of both products and substrates of enzymatic reactions, even if only one of them shows binding with the macrocycle. The latter approach has been utilized in the detection of amino acids even if they show themselves no significant binding to the macrocycle. The corresponding decarboxylases lead to the formation of biogenic amines, whose formation is being detected and can be correlated with the absolute depletion of substrate.[354,457]

8. SUMMARY

Fluorescence detection is well-known for its high sensitivity in photochemistry, analytical chemistry, biochemistry, and beyond. For applications in the environmental and life sciences, the water-soluble fluorescent dyes reviewed here are most relevant. However, the conversion of a fluorescent dye to a chemosensor or chemosensing ensemble requires the introduction of recognition motifs for particular analytes or particular classes of analytes. To the degree that the recognition event is based on a reversible, intermolecular interaction, water-soluble

macrocyclic receptors have become attractive subjects for investigation in combination with fluorescent dyes. The resulting supramolecular host/guest complexes as well as their applications in indicator displacement types of assays have also been examined in detail in this review.

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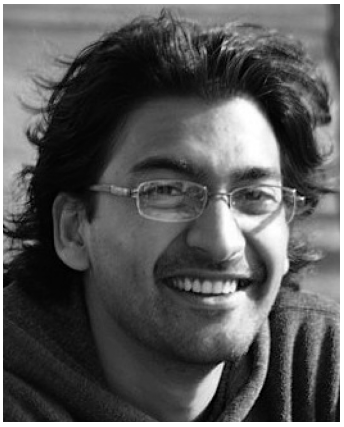
BIOGRAPHIES



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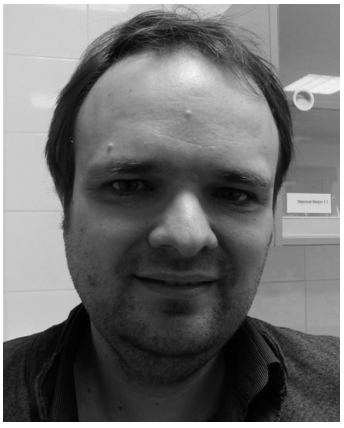

Uwe Pischel was born in Germany, and he obtained his Diploma in Chemistry in 1998 at Humboldt University Berlin and his Ph.D. at the University of Basel, Switzerland, in 2001 with Werner Nau in organic photochemistry. As a postdoc at the Technical University of Valencia, Spain, with Miguel Ángel Miranda in 2002, he was working on stereoselective photoprocesses. In 2003 he moved as Junior Researcher to the University of Porto, Portugal. In 2006 he became Ramón y Cajal Fellow at the Technical University Valencia, Spain, and later on at the University of Huelva, where he has been Lecturer in Organic Chemistry since 2009. He has held visiting professorships at the Jacobs University Bremen, Germany. His research interests are focused on supramolecular chemistry and molecular devices for information processing, with special emphasis on fluorescent systems and their switching.

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ACKNOWLEDGMENT

R.N.D. and W.M.N. acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG Grant NA-686/5-1), the COST Action CM1005 "Supramolecular Chemistry in Water", and the Fonds der Chemischen Industrie. U.P. thanks the Spanish Ministry for Science and Innovation, Madrid (Grant CTQ2008-06777-C02-02/BQU). The authors would also like to thank Bernard Valeur, Jyotirmayee Mohanty, Laszlo Biczók, Anindya Datta, Yu Liu, and Cornelia Bohne for valuable comments on the manuscript.

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