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1,3-Diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline: A Versatile Fluorophore for the Design of Brightly Emissive Molecular Sensors

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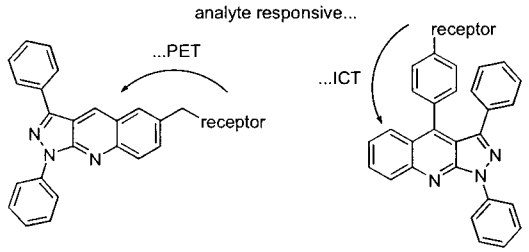
ABSTRACT



The 1,3-diphenyl-1*H*-pyrazolo[3,4-*b*]-quinoline chromophore is a versatile building block for the construction of brightly fluorescent molecular sensors. Facile synthetic procedures allow integration of the chromophore into fluorophore–spacer–receptor systems as well as fluoroionophores operating via intramolecular charge transfer. Whereas the former photoinduced electron-transfer probes show strong analyte-induced fluorescence enhancement, the latter exhibit bright ratiometric dual emission. Employing prototype macrocyclic receptors, the favorable signaling features for metal ion recognition are demonstrated.

Research efforts in the field of molecular sensors indicating chemical stimuli or environmental parameters by a change in their fluorescence properties are still very intensive.[1] In the past few years, besides striving to improve the selectivity of such compounds by advancing the recognition unit, several new directions have been followed to improve their sensitivity.[2] Within the field of fluorescent molecular probe research, modular approaches are especially appealing.[3,4] In an ideal case, such strategies allow compounds to be tailor-made for certain wavelength ranges, analytes, or sensing media by assembling functional units with desired properties from a pool of precursors. Thus, for a successful design, the

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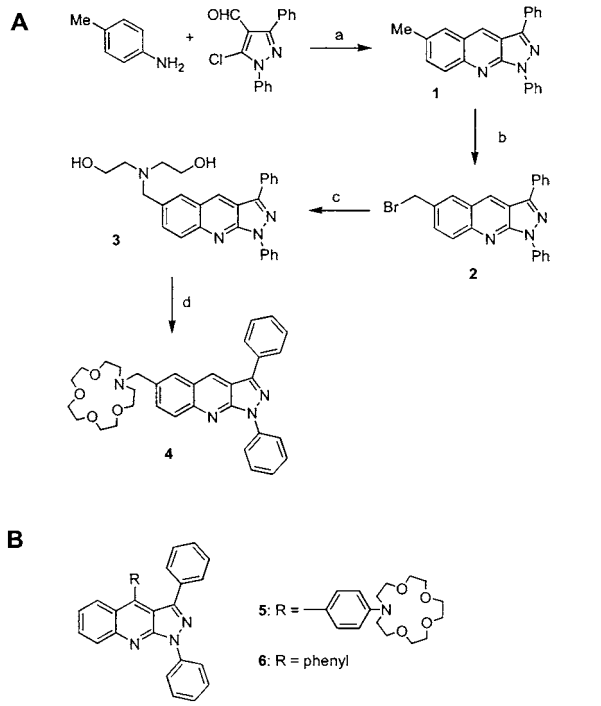
availability of a number of different intercombinable recognition, signaling, and spacer fragments in conjunction with facile synthetic procedures is essential.[5] On the other hand, besides preparative requirements, the key to highly efficient sensing ensembles in terms of signal generation is the choice of an appropriate fluorophore and the control of the active photophysical mechanism.[3d,6]

Based on our work in the area of supramolecular host−guest photochemistry, we are especially interested in rather simple chromophores that can be easily functionalized with different recognition modules in modular architectures.[4c−e,7] One of our main interests here is to design functional dyes that show strong analyte-induced fluorescence enhancement. With regard to the latter, the development of powerful dual emissive probes especially is a central aim.[8] Concerning analyte detection, dual emission, i.e., the occurrence of two spectrally well-separated fluorescence bands that are characteristic for the two states of the sensor molecule, offer the advantage of performing ratiometric sensing. This technique largely avoids errors due to photobleaching or changes of instrumental conditions such as excitation intensity.[9] Our search for a new chromophore capable of invoking dual fluorescence was stimulated by prominent disadvantages disaplayed by many of the systems introduced so far. Often, only one band is highly emissive,[7a,b] the changes are comparatively weak,[10a] or both bands lie largely in the UV spectral region.[10b] In this paper, we introduce the 1,3-diphenyl-1*H*-pyrazolo[3,4-*b*]-quinoline (DPPQ) chromophore[11] as a new versatile building block for photoinduced electron-transfer (PET) and intramolecular charge-transfer (ICT) operative fluorescent probes, in the latter case showing bright dual emission from both fluorescent species. To demonstrate the advantages of the DPPQ unit, we chose widely used receptor units with well-known cation preferences and experimental conditions commonly employed for such combinations of receptor and ion.[1a,b,6,12]

The DPPQ derivatives **4** and **5** were obtained from the respective pyrazole and aniline precursors. As an example, the synthetic procedure for **4** is outlined in Scheme 1. For

Scheme 1. (**A**) Synthesis of 4;[13] (**B**) Structures of **5** and **6**[a]



[a] Key: (a) 180−190 °C, (b) NBS/AIBN/CCl_4, (c) diethanolamine/K_2CO_3, (d) tri(ethylene glycol) di-*p*-tosylate/DMF/NaH (60%).

5,[14] 1,3-diphenyl-5-*N*-phenylpyrazole[15] and 4-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)benzaldehyde[16] were reacted in a final step in the presence of $ZnCl_2$.

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(13) **2**: yellow crystals; mp 204−6 °C; yield 76%. Anal. Calcd for $C_{23}H_{16}BrN_3$: C, 66.68; H, 3.89; N, 10.14. Found: C, 66.41; H, 3.75; N, 10.04. **3**: yellow crystals; mp 134−6 °C; yield 70%; ^{1}H NMR ($CDCl_3$) 8.89 (s, 1H), 8.38 (d, J = 7.7 Hz, 2H), 8.17 (s + d, overlapped, 3H), 7.92 (s, 1H), 7.78 (dd, J = 8.8, 1.6 Hz, 1H), 7.62−7.50 (m, 5H), 7.32 (t, J = 7.14 Hz, 1H), 3.92 (s, 2H), 3.68 (t, J = 5.2 Hz, 4H), 2.82 (t, J = 5.2 Hz, 4H). Anal. Calcd for $C_{27}H_{26}N_4O_2$: C, 73.95; H, 5.98; N, 12.78. Found: C, 73.87; H, 5.88; N, 12.64. **4**: yellow crystals; mp 136−7 °C; yield 22%; ^{1}H NMR ($CDCl_3$) 8.92 (s, 1H), 8.63 (d, J = 7.7 Hz, 2H), 8.17 (d, J = 7.6 Hz, 2H), 8.12 (d, J = 8.8 Hz, 1H), 7.82 (dd, J = 8.9, 1.6 Hz, 1H), 7.62−7.55 (m, 5H), 7.49 (t, J = 7.1 Hz, 1H), 3.88 (s, 2H), 3.71−3.63 (m, 16H), 2.88 (t, J = 5.9 Hz, 4H). Anal. Calcd for $C_{33}H_{36}N_4O_4$: C, 71.72; H, 6.57; N, 10.14. Found: C, 71.65; H, 6.43; N, 10.01.

(14) **5**: yellow crystals; mp 202−4 °C; yield 40%; ^{1}H NMR ($CDCl_3$) 8.60 (d, J = 7.7 Hz, 2H), 8.22 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.75 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.7 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.25−7.18 (m, 3H), 7.11 (d, J = 7.7 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.47 (d, J = 8.8 Hz, 2H), 3.79−3.69 (m, 16H), 3.61 (t, J = 6.1 Hz, 4H). Anal. Calcd for $C_{38}H_{38}N_4O_4$: C, 74.25; H, 6.23; N, 9.11. Found: C, 74.31; H, 6.21; N, 8.88.

For the fluorophore−spacer−receptor dye **4**, the negligible influence of the electron-donating macrocyclic recognition unit on the energetics of the optical transitions within the DPPQ chromophore follows from a comparison of **4** with model compound **6**.[18] For instance, the maxima of the absorption and fluorescence bands of **6** were found at 396 and 485 nm in acetonitrile,[19] while those of **4** are centered at 398 and 480 nm in this solvent. The moderate increase in Stokes shift as a function of solvent polarity, from 2600 to 4180 cm^{-1} upon going from hexane to acetonitrile, indicates the partial charge-transfer character of the transition within the asymmetric pyrazoloquinoline fragment. (Details on the photophysical mechanisms of the unbound dyes as well as the host−guest ensembles will be published separately.[20]) In contrast, the reduced fluorescence quantum yield Φ_f of **4** as compared to **6**[19] and especially the strong decrease of Φ_f of **4** with increasing solvent polarity (Table 1) suggest that quenching via an electron-transfer process from the methylene spacer-appended and electronically decoupled amino nitrogen atom to the chromophore is accelerated as the solvent polarity increases. The biexponential decays, with relative amplitudes varying only slightly over the entire emission band, observed for **4** in the medium to highly polar solvents are tentatively attributed to the existence of two different ground-state conformers, related to the endo/exo isomerism.[21] Differing in the degree of pyramidalization of the amino nitrogen atom as well as the position and direction of the lone electron pair with respect to the chromophore π-system, these conformers can vary in their PET quenching activity.[4c,7a]

Table 1. Selected Spectroscopic Data of **4** and **5** as well as Their Na^I and Ca^{II} Complexes at 293 K[a]

	solvent	λ_{abs}/nm	λ_{em}/nm	Φ_f	τ_f/ns
4	MeOH	398	482	0.031	0.8[b]
4	MeCN	398	480	0.022	1.3[b]
4	THF	402	470	0.040	0.8[b]
4	Et_2O	401	453	0.30	8.3[b]
4	hexane	403	444	0.54	11.7
4-Na^I	MeCN	400	482	0.39	17.9
4-Ca^{II}	MeCN	400	486	0.42	20.1
5	MeCN	413	593	0.18	1.0, 10.0[c]
5	THF	416	525	0.35	1.5, 8.2[c]
5	Et_2O	413	488	0.34	1.3, 5.1[c]
5	hexane	417	445	0.37	4.7
5-Na^I	MeCN	401	584	0.20	2.9, 10.0[c]
5-Ca^{II}	MeCN	398	498	0.35	3.2, 14.2[c]

[a] $c_{dye} = 5 \times 10^{-6}$ M, $\lambda_{exc} \sim 390$ nm. The coordination features of the complexes are consistent with those reported on related compounds containing these receptors.[1a,17] [b] Mean lifetime of a biexponential decay with 0.6, 20.8 (MeOH), 0.4, 17.9 (MeCN), 0.8, 18.2 (THF), and 1.6, 9.3 ns (Et_2O), determined by global analysis; see text. [c] For the wavelength dependence of the sign of the amplitude of the short lifetime, see text.

The high similarity of the absorption data of **4** and **5** shown in Table 1 reveals the suitability of both design concepts for largely decoupling the chromophore and the receptor unit in the ground state, i.e., separation of the two modules either by a σ-spacer or by a perpendicular arrangement. However, upon excitation, the features of **5** are markedly different from those of PET-active **4**. The insensitivity of the absorption band position on solvent polarity and the contrasting strong increase in Stokes shift (from 1830 cm^{-1} in hexane to 7750 cm^{-1} in acetonitrile) suggest that the dipole moment of the emitting state in polar solvents is much higher than that of the ground state (of **5**) and of the emissive state of **4**. Accordingly, emission of **5** in polar solvents can tentatively be attributed to originate from a radiative charge recombination process as a consequence of a charge transfer from the anilino donor to the DPPQ moiety, acting as an electron acceptor, rather than from a transition within the DPPQ fragment.[19,22] This assumption is supported by the time-resolved data in Table 1. Here, the fast component of a biexponential decay is found as a decaying species in the high-energy and as a rise time in the low-energy part of the emission spectrum (obtained by global analysis, cf. ref 7a). An outstanding feature of **5** is the high fluorescence yield of the CT species, exemplified by $\Phi_f = 0.18$ in acetonitrile as compared to 0.37 in hexane. For many other related biaryl-type donor−acceptor dyes, the CT state is only weakly or nonfluorescent and can thus not be exploited for signaling applications relying on a dual mode transduction mechanism.[7a−d,23] This strong CT fluorescence is probably connected with an allowed emissive character of this state. Often, CT states are of the 'twisted intramolecular charge transfer' (TICT) type[24] with inherent forbidden emissive properties. The allowed emissive properties of **5** are thus most probably due to a relaxation toward planarity in the excited state. There are a number of compound classes where allowed and forbidden ICT states have been identified.[22,25]

The remarkable features of the PET and ICT processes of the 4- and 6-donor-substituted DPPQ derivatives suggest that these dyes can yield favorable effects in the presence of analyte species that are readily bound by the macrocyclic units. To demonstrate the basic sensing mechanisms, we investigated the spectroscopic properties of **4** and **5** in the

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presence of two representative main group metal ions, Na^{I} and Ca^{II}, in acetonitrile. Upon cation addition to **4**, the changes in spectral band position are comparatively small (Table 1), in agreement with a PET signaling mechanism.[1a] Binding of a cation to the receptor strongly alters its redox potential and weakens its donor strength thus decelerating the quenching process. As a result, the fluorescence strongly increases. Moreover, an advantage of the choice of a receptor with a trialkylamino nitrogen atom is directly evident from the nearly identical fluorescence enhancement factors found for Na^{I} as well as Ca^{II}, the former being a weakly *N*-binding cation commonly yielding only moderate switching effects.[4c,7a,c]

As follows from Figure 1 and Table 1, equipping the DPPQ fluorophore with a 4-(*p*-phenyl) receptor moiety as

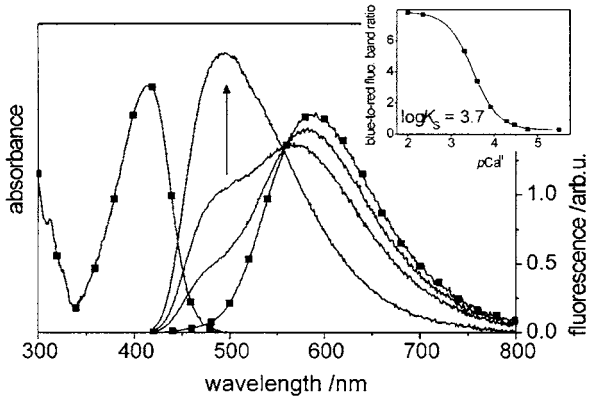

Figure 1. Steady-state spectra of **5** (■) and fluorescence titration with Ca^{II} in acetonitrile ($c_{dye} = 5 \times 10^{-6}$ M, $\lambda_{exc} = 390$ nm).

in **5** can yield dual emissive sensor molecules with a high fluorescence output for both states of the system, bound and unbound. Furthermore, the strong CT character combined with mesomeric interaction in **5** leads to the fact that both bands are well-separated and cover a broad range of the visible spectrum, between 440 and 700 nm (Figure 1). Besides the strong influence of the valence and electron affinity of the cation on the band position of the complex's fluorescence spectrum (cf. shifts induced by Na^{I} as compared to Ca^{II}, Table 1), a biexponential decay behavior is observed for these complexes, where the amplitude of the fast component is positive in the blue and negative in the red part of the spectrum and its weight always smaller than −50%. These excited-state features can be either due to two ground-state conformers[7a] or an excited-state branching. In the first case, upon excitation, one conformer relaxes slower toward a more planar structure, accompanied by a subsequent charge-transfer and internal decoordination reaction to [**5*** − $M^{I/II}$].[6a] In the latter type of reaction, one part of the precursor state relaxes to CT ultrafast, whereas the other part relaxes toward the minimum of the precursor state and then has a barrier to reach CT, which slows down the reaction as was shown by us for a twisted biphenyl derivative.[26]

Concerning the development of DPPQ-based probes for analytical applications in real-life media, first results obtained for **4**/Ca^{II} and **5**/H^{+} in protic and mixed aqueous solvents are very promising (e.g., **4**-Ca^{II} in MeOH again displays enhanced fluorescence with PET-like features of $\Phi_f = 0.26$ and $\tau_f = 13.2$ ns). Thus, for instance, targeting Ca^{II}, the use of selective receptors with a donor atom that can actively participate in both, binding and signaling,[27] should yield suitable molecular Ca^{II} sensors of the PET and/or ICT type introduced here.[28] Accordingly, the preparation of such compounds is currently in progress.

In conclusion, we have shown that the DPPQ chromophore is a promising candidate for the construction of brightly signaling fluorescent probes, relying either on an intramolecular charge or electron transfer process. The strong dual fluorescence resulting from the ICT process especially is an advantageous feature in terms of ratiometric fluorosensing in the visible spectral region. Moreover, the modular design of functionalized pyrazoloquinolines promises to conceive tailor-made fluoroionophores with purpose-fit signal expression and cation selectivities by introducing the respective spacers and recognition modules.

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