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Dye Deaggregation

Strongly Fluorescent, Switchable Perylene Bis(diimide) Host–Guest Complexes with Cucurbit[8]uril In Water**

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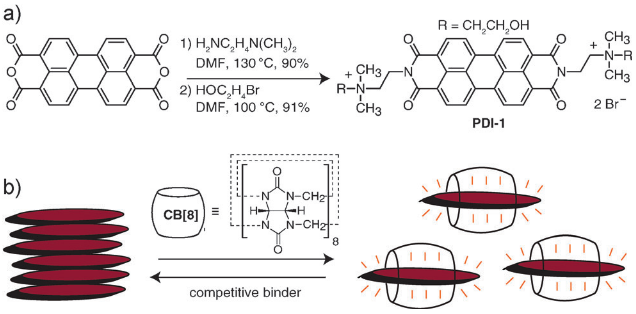
Water-soluble fluorescent dyes have found widespread use in synthetic materials as well as in both in vivo and in vitro biological applications.[1–3] In particular, readily accessible, strongly absorbing, photostable dyes that emit with high quantum yield in the visible region are desirable. Unfortunately, conventional fluorophores (such as aromatic hydrocarbons) are hydrophobic and have a high propensity towards aggregation, eximer formation, and unspecific adsorption in aqueous solutions, all of which are detrimental for most applications. Prime examples are perylene bis(diimide) (PDI) dyes, which are excellent fluorophores; they have been used as pigments and colorants for decades on account of their excellent photophysical and thermal stability.[4] Unfortunately, they tend to form non-fluorescent π-π stacks in water,[5,6] which greatly limits biological applications based on confocal microscopic or single-molecule spectroscopic techniques.

To increase aqueous solubility, the side-group functionalization of PDI dyes,[6,7] mainly through the introduction of hydrophilic substituents at the diimide positions,[8–14] has become a popular strategy. This process results in additional applications, ranging from fluorescent labels[15] and sensors[16–18] to dye lasers,[19] as well as producing molecular building blocks for switches,[20] supramolecular/polymeric assemblies,[21–24] and molecular wires.[12,25] In most cases, the fluorescence emission has remained low, likely on account of π–π stacking. However, some derivatives can become highly fluorescent under the deaggregating conditions of high dilution.[26] To efficiently suppress aggregation, steric encumbrance introduced by substituents in the "bay region"[26–28] or large dendrons at the diimide sites[29,30] are generally required, which is substantially more demanding from the synthesis and purification point of view.

Herein, we establish a supramolecular approach to prevent PDI dyes from aggregating in aqueous solution by forming a strong host–guest inclusion complex with the macrocyclic host cucurbit[8]uril (CB[8]). In contrast to covalent modifications, the reversibility of the host–guest complex formation also allows for stimuli-responsive switching of the photophysical properties of PDI.

CB[7], a smaller member of the cucurbit[*n*]uril family ($n = 5$–8, 10), is well known to form 1:1 complexes with a range of organic fluorophores, such as rhodamines.[31–35] In some cases, dye encapsulation resulted in profound changes in the emission wavelength and quantum yield, as well as increased photostability.[1] As CB[8] has a larger cavity, it can simultaneously bind two planar aromatic molecules, typically a dicationic first guest, such as dimethylviologen (MV), and an electron-rich second guest, such as 2,6-dihydroxynaphthalene.[36,37] CB[8]-templated 1:1:1 ternary complexes have been exploited for materials assembly[38–41] with the macrocycle acting as a supramolecular "handcuff", but fluorescent first guests for CB[8] have remained scarce to date.[42]

Water-soluble **PDI-1** was synthesized from perylene bis(anhydride) in two steps with high yield and purity (Scheme 1a). Broad peaks in the ^{1}H NMR spectrum, a strongly quenched fluorescence, as well as characteristic features in the UV/Vis absorption bands,[6] all confirmed that the ionic groups at the diimide positions alone were insufficient to suppress π aggregation of **PDI-1** in water (Figure 1). Aggregation was also observed by dynamic light scattering (DLS) and Scanning Electron Microscopy (SEM) experiments (Supporting Information, Figure S1). Based on space-filling models from DFT calculations (Figure S2), CB[8] should be capable of complexing **PDI-1**, whereas the cavities of the smaller CB[*n*] homologues are too small. Indeed, the addition of excess CB[8] to a non-fluorescent, aqueous **PDI-1** solution (20 μM) resulted in a dramatic increase in fluorescence intensity (Figure 1b and Figure S3), whereas addition of CB[7] did not cause significant changes (Fig-



Scheme 1. Synthesis and aggregation properties of **PDI-1**. a) Two step synthesis of **PDI-1**. b) Reversible deaggregation of **PDI-1** stacks in water upon addition of CB[8].

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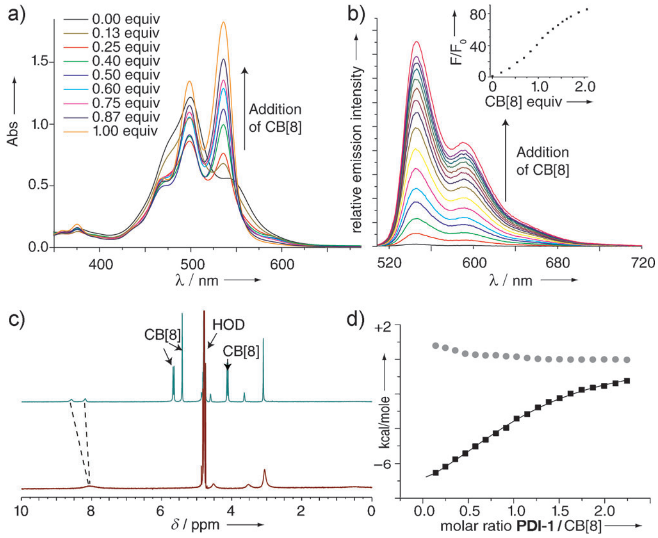

Figure 1. Analytical data for **PDI-1** complexes with CB[8]. a) UV/Vis absorption spectra and b) fluorescence spectra for **PDI-1** (20 μM in H_2O) upon addition of CB[8]. The inset shows the total fluorescence with increasing CB[8] concentration. c) ^1H NMR (D_2O) spectra of **PDI-1** (0.5 mM) prior (bottom) and after (top) addition of 1 equiv CB[8]. d) Integrated heats of injection for ITC titration of **PDI-1** (200 μM) into a CB[8] solution (1.42 mL, 20 μM; ■) as compared to titration into water (1.42 mL; ●). All experiments were conducted at 25 °C. See the Supporting Information for details.

ure S4). The **PDI-1**·CB[8] complex fluoresces with almost unit quantum yield (0.90 ± 0.10), whereas that of the free dye is very low (ca. 0.03) under the same conditions (see the Supporting Information for details), which presumably corresponds to a residual fraction of non-aggregated monomeric dye. Also, the emission lifetime of **PDI-1** increased from 4.45 ns to 5.88 ns upon CB[8] addition, which is characteristic for complexation of fluorescent dyes by macrocycles, particularly CBs.[1] The hyper- and hypsochromic shifts of the 0–0 absorption band (Figure 1 a) provide another spectral signature for the deaggregation and monomerization of the PDI chromophore upon addition of CB[8].

The photostability of the **PDI-1**·CB[8] complex was determined relative to rhodamine 6G (Rh6G) and its CB[7] complex as standards. The resulting photodecomposition quantum yield was found to be $(2.0 \pm 0.5) \times 10^{-7}$, which is about five times lower than Rh6G and similar to that of Rh6G·CB[7] (see the Supporting Information for details).[31] As a consequence, the photostability of the **PDI-1**·CB[8] complex falls in the range of the most photostable water-soluble fluorescent dyes.[31]

The addition of CB[8] to a solution of **PDI-1** in D_2O resulted in a sharpening and downfield shift of the aromatic **PDI-1** peaks in the ^1H NMR spectrum (Figure 1 c). It is important to note that the downfield shift upon **PDI-1**·CB[8] complex formation results from a combination of two competing effects. Deaggregation of PDI is known to result in a downfield shift,[5] whereas the encapsulation of hydrophobic moieties inside the cavity of CB[8] usually leads to an upfield shift.[43] Further confirmation of **PDI-1**·CB[8] complexation was provided by pulse field-gradient (PFG) NMR spectroscopy, which displayed the same diffusion rates for **PDI-1** and CB[8] in an equimolar mixture. Thus, both **PDI-1** and CB[8] diffuse together as one entity (Figure S6). ESI-MS measurements are also consistent with the proposed 1:1 complex stoichiometry of CB[8] to **PDI-1** (Figure S7). To obtain an estimate of the association strength between **PDI-1** and CB[8], isothermal titration calorimetry (ITC) was employed; titration of **PDI-1** into a CB[8] solution resulted in a strongly exothermic isotherm whereas titration of **PDI-1** into water is slightly endothermic (Figure 1 d). A K_a value of ca. $10^5\,\text{M}^{-1}$ for the **PDI-1**·CB[8] complex was obtained through fitting of the binding isotherm to a 1:1 complexation model, after correction for the heats of dilution.

It should be pointed out that, although **PDI-1** carries a double cationic charge, as is the case for most high-affinity CB[8] binders, such as viologen derivatives[36,44] and tetramethyl benzobis(imidazolium) MBBI,[42] the positive charge centers of **PDI-1** are quite distant and not in conjugation with the PDI core. Thus, electrostatic interactions between the alkylammonium groups and the partial negatively charged CB[8] cavity[44,45] and portals are likely not the only reason for the high binding affinity. Interestingly, when the smaller PDI analogue naphthalene diimide (NDI) was introduced to a solution of CB[8], no complexation was observed. The steric clash of the carbonyl-fringed CB[8] portal and the NDI carbonyl groups is likely the reason for the inability of CB[8] to bind NDI guests (see the calculated geometry for the **PDI-1**·CB[8] complex in Figure S2).

Our host–guest encapsulation strategy offers a much more straightforward approach to protect the PDI dye from self-aggregation than arduous synthetic modifications of the dye. Importantly, the method also offers the opportunity to reversibly switch the fluorescence response through additional chemical stimuli. For example, when 1.0 equiv of the strong, competitive guest adamantine amine is added to the **PDI-1**·CB[8] complex, the fluorescence is instantly turned off (Scheme 1 b and Figure S8). This is consistent with sequestration of adamantine amine by CB[8] and reaggregation of the uncomplexed **PDI-1**. The addition of excess CB[8] restores the fluorescence.

PDI is a good electron acceptor, which is capable of undergoing many reduction–oxidation cycles without structural degradation, a property that accounts for its frequent use in organic-photovoltaic applications. Both electrochemical and chemical reduction of PDI derivatives with sodium dithionite ($Na_2S_2O_4$) have been described in the literature.[46,47] Indeed, when the **PDI-1**·CB[8] complex was treated with $Na_2S_2O_4$, the characteristic blue color of reduced **PDI-1** appeared (Figures S9 and S10) and the solution became non-fluorescent. Re-oxidation with air restored the UV/Vis and fluorescence features of the **PDI-1**·CB[8] complex. Thus, **PDI-1**·CB[8] can be employed as a fluorescent redox reporter. The reduction–oxidation cycles can be repeated many times, limited only by the increase in ionic strength (cations bind competitively to the CB[8] portals, resulting in dissociation of the **PDI-1**·CB[8] complex, see inset in Figure S10). Cyclic voltammetry (CV) experiments carried out on **PDI-1** and **PDI-1**·CB[8] solutions revealed that the latter can be cycled five times with only minor changes in the cyclic voltammogram, whereas **PDI-1** results in dye deposition on the electrodes (Figure S11). This further demonstrates the utility of CB[8], which can act to protect the dye from its surrounding medium and to beneficially affect its properties.

Although **PDI-1** does not form 2:1 complexes with CB[8] on account of its size, there is still enough space in the cavity of the **PDI-1**·CB[8] complex to bind smaller aromatic molecules. For example, addition of dicationic aromatic compounds, such as MV or *N*,*N*′-dimethyldipyridyliumethylene (MDiPyEt) resulted in the formation of a 1:1:1 ternary complex with quenched fluorescence and pronounced changes in the UV/Vis spectra (Figure S12). Such competitive titrations can be conveniently employed to determine the K_a values for the ternary complexes; the resulting values were in good agreement with those from ITC (Table 1).

Table 1: Thermodynamic data for **PDI-1**·second-guest·CB[8] ternary complex formation in H_2O at 25 °C.

second guest[a]	K_a [10^4 M^{-1}][b]	K_a [10^4 M^{-1}][c]	ΔH [kJ mol^{-1}][c]	$-T\Delta S$ [kJ mol^{-1}][c]
MDiPyEt	50 ± 10	51 ± 3	−5.4 ± 0.1	−2.4 ± 0.2
MBBI	50 ± 10	26 ± 2	−3.9 ± 0.1	−3.5 ± 0.3
MV	30 ± 10	16 ± 2	−3.3 ± 0.1	−3.8 ± 0.3
DBF-PEG	4 ± 1	2.6 ± 0.3	−11.6 ± 0.2	5.5 ± 0.4
AzoB-PEG	4 ± 1	1.7 ± 0.2	−16.6 ± 0.2	10.9 ± 0.4
BiPh-PEG	3 ± 1	0.62 ± 0.03	n.a.	n.a.
Ant-PEG	0.9 ± 0.2	0.39 ± 0.03	n.a.	n.a.

[a] See text for full names. [b] From UV/Vis titrations at a **PDI-1**·CB[8] concentration of 20 μM. [c] From ITC titrations of second guest (1 mM) into **PDI-1**·CB[8] (100 μM). Mean errors from two repetition experiments are given. n.a. = not applicable.

Strikingly, **PDI-1** behaves as both a typical first and second guest for CB[8]; electron-rich aromatic compounds, such as dibenzofuran (DBF), azobenzene (AzoB), biphenyl (BiPh), and anthracene (Ant), showed characteristic features of ternary complexes with **PDI-1**·CB[8] in fluorescence, ^{1}H NMR, UV/Vis, and ITC studies (Figures S13–S29). In order to perform quantitative titration studies, these second guests were covalently linked to poly(ethylene glycol) (PEG) to provide sufficient solubility in water.[42,48] Nevertheless, the small molecule second guests could be solubilized by the **PDI-1**·CB[8] complex alone (Figure S21 shows the UV/Vis spectra for the **PDI-1**·azobenzene·CB[8] complex as a representative example). Interestingly, each of the **PDI-1**·second-guest·CB[8] ternary complexes showed characteristic features in the UV/Vis spectra, such as an emergent red-tailing shoulder, which suggests that specific interactions, such as charge transfer (CT), occur between **PDI-1** and the second guests. CT bands have also been documented for MV·second-guest·CB[8] ternary complexes, but only at substantially higher concentrations (typically 1–2 orders of magnitude difference, for example, 20 μM compared to ≥ 0.5 mM).[36,44]

The **PDI-1**·CB[8] complex appears to be more selective towards the electron-rich second guests that it binds than MV·CB[8] and other reported dicationic first guest CB[8] complexes. For example, whereas naphthols were generally found to be tight binders for MV·CB[8], only very weak ternary complexes could be detected for 2,6-dihydroxynaphthalene, 2-naphthol, or 2-naphthol-PEG with **PDI-1**·CB[8], as measured by UV/Vis, fluorescence, and ITC (see the Supporting Information). Other typical second guests for MV·CB[8], such as sesamol and phenol, also displayed extremly weak binding with **PDI-1**·CB[8].

Switchable supramolecular assemblies have attracted vast interest in the literature on account of access to novel materials properties.[49–52] In an effort to compare a non-covalent host–guest binding strategy with a covalent approach, PDI was flanked with PEG chains through a copper-catalyzed azide-alkyne cycloaddition (CuAAC) to form a PEG-PDI-PEG structure, as illustrated in Figure 2 a.

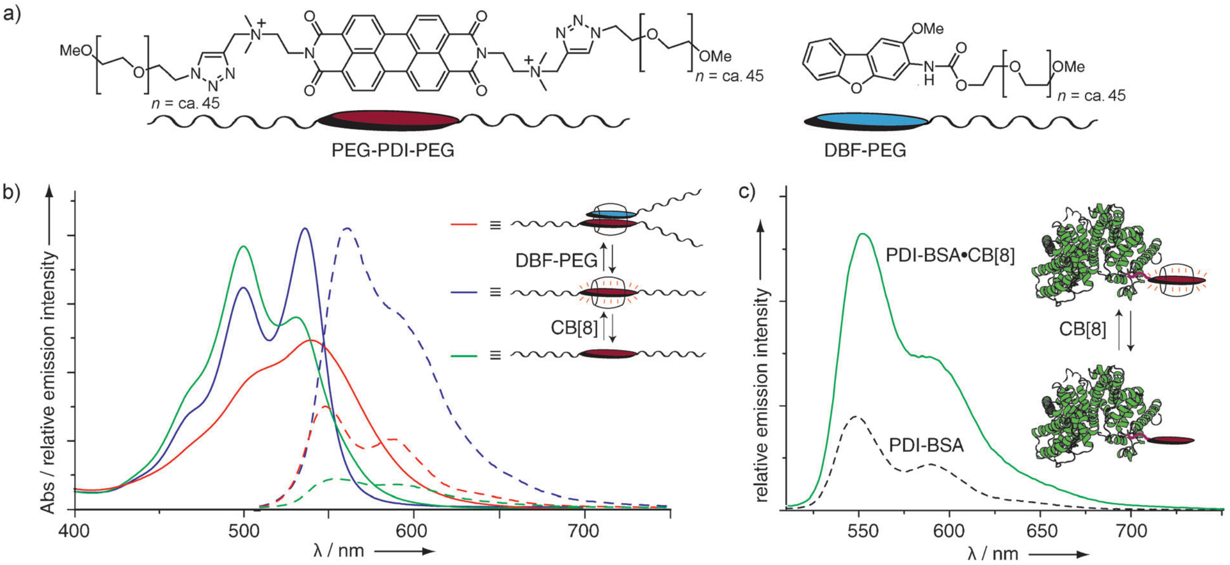

Figure 2. Binding studies for macromolecular guest molecules. a) Chemical structures of PEG-PDI-PEG and DBF-PEG. b) Absorption and emission spectra of PEG-PDI-PEG, PEG-PDI-PEG·CB[8] and PEG-PDI-PEG·DBF-PEG·CB[8] (20 μM in each component). c) Emission spectra for BSA-PDI (20 μM) prior to and after addition of solid CB[8] (2.5 equiv).

To a certain extent (similar to the effect of dendron attachment),[29] PEG prevents the self-aggregation of the PDI-core, which is evidenced by the higher emission intensity of PEG-PDI-PEG than of **PDI-1** in water alone. Nevertheless, addition of CB[8] to an aqueous solution of PEG-PDI-PEG showed an additional six-fold increase in the relative quantum yield. This finding indicated that the CB[8] can thread the PEG chain and reach the PDI unit, and was further supported by ^{1}H NMR experiments displayed in Figure S29, showing a broadening of the CB[8] peaks and the typical shift of the PDI peaks. Consequently, this structural design allows for the formation of a supramolecular three-armed polymer by ternary complex formation. Indeed, addition of DBF-PEG to the PEG-PDI-PEG·CB[8] pseudo-rotaxane complex resulted in an immediate quenching of the fluorescence, the appearance of a red-tailing CT shoulder in the UV/Vis spectrum (Figure 2b), and shifting of both the CB[8] and aromatic peaks in the ^{1}H NMR (Figure S30).

Finally, chemical functionalization of **PDI-1** with methacrylate groups (see the Supporting Information for details) allowed for the labeling of a protein, bovine serum albumin (BSA), with the PDI dye through a thiol–ene reaction analogous to literature procedures.[41] An increase in the fluorescence emission intensity of the dye-labeled BSA was observed when CB[8] was added (Figure 2c). Therefore, the host–guest complexation of PDI dyes with CB[8] is not only feasible for small molecule and synthetic polymer systems, but should also be applicable to the fluorescent labeling of biomacromolecules. In this context, CB[8] not only prevents self-aggregation of the PDI dye, but can also suppress unwanted interactions between the fluorophore and the surrounding environment.

In conclusion, we have demonstrated a facile supramolecular approach for the use of PDI dyes as fluorophores in aqueous media through the elimination of self-aggregation. Specifically, the macrocyclic host, CB[8], can encapsulate PDI inside its cavity, leading to a dramatic increase in the fluorescence quantum yield of the dye while ensuring high photochemical and chemical stability of the PDI dye. The method retains the spectral properties of the parent PDI chromophore and offers opportunities for versatility through labeling of the diimide functional groups. Furthermore, these complexes were shown to be stimuli-responsive to competitive binders and can be (electro)chemically switched between the non-fluorescent reduced states and (re)oxidized fluorescent states. Moreover, addition of suitable dicationic or electron-rich second guests leads to the formation of 1:1:1 ternary complexes, which can be utilized for the reversible formation of higher-order supramolecular architectures in water.

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