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VIP

A Crown Ether Decorated Dibenzocoronene Tetracarboxdiimide Chromophore: Synthesis, Sensing, and Self-Organization

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Abstract: A macrocyclic dibenzocoronene tetracarboxdiimide containing two benzo-21-crown-7 groups has been synthesized. It shows liquid-crystalline behavior and selectively binds Pb^{2+} or K^{+} to form 1:2 complexes in solution. The complexation leads to a significant increase of fluorescence; the surface organization of discotic columnar structures, in the solid-state, can be controlled by selective ion binding.

Perylenediimides (PDIs) and their core-expanded analogs have found widespread applications,[1–10] as these fluorescent dyes are readily accessible, strongly absorbing, and highly photostable. However, owing to π–π stacking, they have a great tendency to aggregate in solution. Suppressing the aggregation is essential, considering the highly desirable applications of these dyes as fluorescent probes. Instead of introducing bulky groups (e.g. large dendrons) in the "bay region"[13a,b] or at the diimide terminus by tedious synthesis, control over non-covalent interactions by specific external stimuli can not only provide a facile way to prevent dyes from aggregating, but also create stimuli-responsive materials.

Dibenzocoronene tetracarboxdiimide[11] (dibenzo-CDI), representing a bay-extended PDI, easily forms aggregates in solution due to its large aromatic π-system. It is a promising candidate to create stimulus-responsive fluorescent materials, because its aggregates can be reversibly changed to dissociated molecules accompanied with enhanced fluorescence.[12] On the other hand, benzo-21-crown-7 (B21C7) has been intensively investigated in supramolecular chemistry. Various rotaxanes[15b] and supramolecular polymers[15c–f] have been constructed using B21C7 as an adaptive host molecule. In view of its unique binding properties, the introduction of B21C7 into PDIs will endow PDIs with efficient binding groups that can selectively encapsulate metal ions. Herein, we report a bay-extended PDI, namely, dibenzocoronene tetracarboxdiimide **1** (dibenzo-CDI **1**), which bears two B21C7 groups at the periphery. The incorporation of flexible B21C7 groups not only controls the thermotropic behavior but also imparts a high affinity to metal ions. The non-covalent interaction between crown ether motifs and metal ions readily tunes the optical properties as well as the self-organization behavior of **1**.

The synthetic route toward dibenzo-CDI **1** is shown in Scheme 1. The bromo-B21C7 (**5**) was prepared according to the typical cyclization method.[15a] **5** was then treated with bis(pinacolato)diboron to obain the corresponding boronic ester (**4**). The boronic ester **4** was further treated with 1,7(6)-dibromoperylenetetracarboxdiimide **3** through Suzuki coupling to afford PDI derivative **2** in 90% yield. Although dibromoperylenetetracarboxdiimide **3** usually contains 1,7- and 1,6-isomers, which are hard to separate,[11] the resulting PDI derivative **2** (mixture of 1,7- and 1,6-isomers) generated the same product **1** upon cyclodehydrogenation. The crown ether-substituted PDI **2** was further cyclodehydrogenated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in dry dichloromethane at 0 °C,[11] affording the target dibenzo-CDI **1**, which was highly soluble in common organic solvents such as dichloromethane, chloroform, toluene, and THF, but hardly soluble in acetonitrile, acetone, and methanol. UV-Vis and fluorescence spectra of dibenzo-CDI **1** were recorded in CHCl$_3$ (see Figure S7 in the Supporting Information, ESI). Dibenzo-CDI **1** displayed sharp absorption bands at 364, 499 and 549 nm. Upon excitation at 365 nm, it emitted a bright yellow fluorescence with a maximum at 571 nm.

Bearing a large rigid benzocoronene core, dibenzo-CDI **1** tends to form aggregates in solution upon addition of poor solvents. Due to the aggregation-caused quenching effect, the fluorescence of **1** is expected to be severely decreased.[12] For example, the dilute solution (10 μM) of dibenzo-CDI **1** in chloroform is highly luminescent. Upon addition of a poor solvent (e.g. acetonitrile) to the chloroform solution, a significant decrease of fluorescence intensity was observed (Figure 1). Additionally, absorbance changes were observed, including peak broadening, a decrease in intensity, and an

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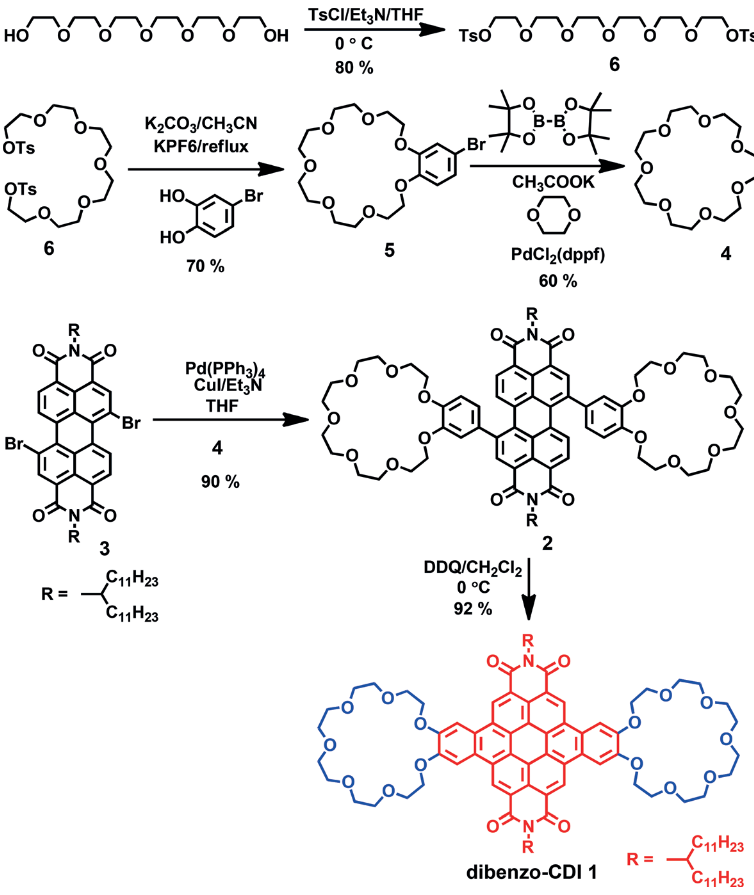

Scheme 1. Synthesis of dibenzocoronene tetracarboxdiimide (dibenzo-CDI **1**).

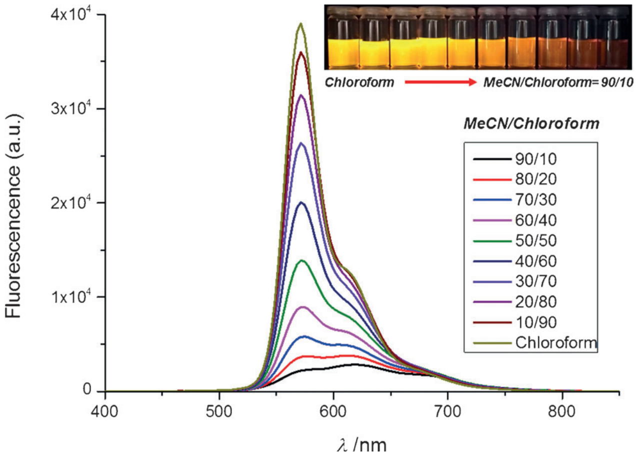

Figure 1. Fluorescence emission spectra of dibenzo-CDI **1** in chloroform and MeCN, $\lambda_{ex} = 365$ nm, [dibenzo-CDI **1**] $= 1.00 \times 10^{-5}$ M. The inset shows a photograph of dibenzo-CDI **1** in chloroform and MeCN under UV-light irradiation.

overall hypsochromic shift (Figure S8, Supporting Information). These changes indicated the overlapping of benzocoronene chromophores to form J-type aggregates.

The two B21C7 groups of dibenzo-CDI **1** serve as a cation-receptor. We initially investigated the fluorescence changes after binding heavy metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) in organic solution ($CHCl_3/CH_3CN = 1{:}1$, v/v). Addition of two equivalents of Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, or Hg^{2+}, exerted only little effect on the emission of dibenzo-CDI **1** (see Figure S8 in the Supporting Information). However, a remarkable change was observed upon addition of Pb^{2+}, the fluorescence intensity was significantly increased.

We then further investigated the fluorescence response of dibenzo-CDI **1** by varying the concentrations of Pb^{2+} (0–120 μM) to obtain quantitative information on the binding stoichiometry (see Figure S9 in the Supporting Information). Upon addition of Pb^{2+}, the fluorescence of dibenzo-CDI **1** gradually increased and saturated when reaching two equivalents of Pb^{2+}. This indicates the formation of a 1:2 complex between dibenzo-CDI **1** and Pb^{2+}. A mole ratio plot for the complexation further confirmed a 1:2 stoichiometry (see Figure S10 in the Supporting Information). To obtain detailed information on the association constant between dibenzo-CDI **1** and Pb^{2+}, isothermal titration calorimetry (ITC) was performed (see Figure S14 in the Supporting Information). Titration of Pb^{2+} into the solvent ($CHCl_3/CH_3CN = 1{:}1$, v/v) was slightly endothermic, however, addition of Pb^{2+} to a dibenzo-CDI **1** solution resulted in a strongly exothermic isotherm. An association constant (K_a) value of $6.59\ (\pm 0.13) \times 10^4\ \mathrm{M}^{-1}$ for the dibenzo-CDI **1** 2[Pb^{2+}] complex was obtained through fitting of the binding isotherm to a 1:2 complexation model.

To shed more light on the complexation, the ^{1}H NMR spectra of dibenzo-CDI **1** were analyzed both in the absence and presence of Pb^{2+} (Figure 2). After addition of Pb^{2+} to dibenzo-CDI **1** in a ($CDCl_3/CD_3CN = 1{:}1$, v/v) mixture, the resonance of protons Ha–Hh shifted downfield due to complexation. In addition, the signals of protons Hc–Hg on the two crown ether rings broadened. Evidently, the crown ether rings of dibenzo-CDI **1** bind Pb^{2+} in organic solution to form a 1:2 complex. Upon complexation with Pb^{2+}, the steric hindrance between Pb^{2+} resulted in disaggregation of dibenzo-CDI **1**. The disaggregation led to a downfield shift of proton signals of **1** and a fluorescence enhancement of

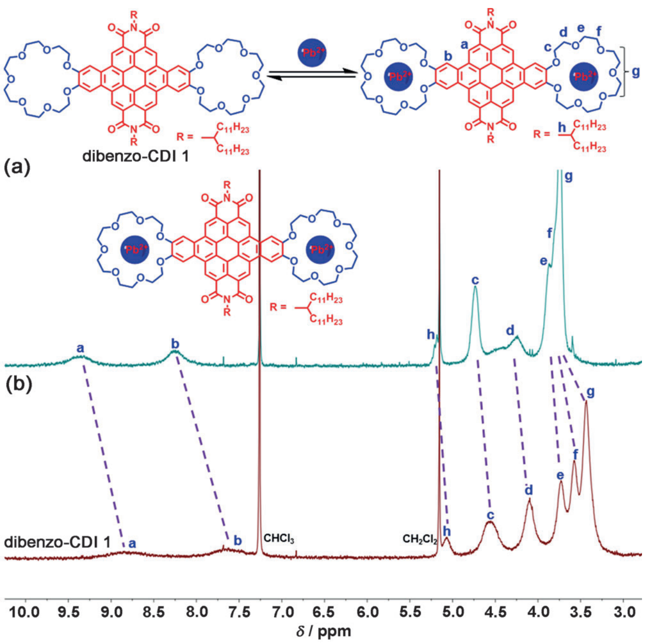

Figure 2. ^{1}H NMR spectra ($CDCl_3/CD_3CN$ 1:1, 293 K, 250 MHz) of (a) 4.00 mM dibenzo-CDI **1**+8.00 mM Pb^{2+}; (b) 4.00 mM dibenzo-CDI **1**.

about 37 %. Therefore, dibenzo-CDI **1** can work as a “turn-on” probe for Pb^{2+}.

As expected, dibenzo-CDI **1** also binds K^+ owing to the high affinity of B21C7 for K^+.[15a] The 1:2 stoichiometry was confirmed by the mole ratio plot, based on fluorescence data (see Figures S11–S12 in the Supporting Information). The K_a of the complex dibenzo-CDI **1** 2[K^+] was determined by ITC to be 2.28 (±0.36) × 10^4 M^{-1} (see Figure S15 in the Supporting Information). Binding K^+ also enhances the fluorescence of dibenzo-CDI **1** and makes the resonances of corresponding protons on dibenzo-CDI **1** shift downfield (see Figure S17 in the Supporting Information). When two equivalents of K^+ were added to dibenzo-CDI **1** in $CHCl_3/CH_3CN$ (1:1, v:v), the fluorescence intensity of **1** increased by 31 %, which was smaller than that of adding Pb^{2+} under identical conditions (see Figure S16 in the Supporting Information). This result is consistent with the smaller binding constant of K^+ compared with that of Pb^{2+}. Furthermore, K^+ can be excluded from the crown ether binding site of **1** by adding a competitive host of 18-crown-6, which has a higher affinity for K^+ compared with that of B21C7.[11c] When two equivalents of 18-crown-6 were added to a solution of **1** (100 μM) and K^+ (200 μM) in $CHCl_3/CH_3CN$ (1:1), the original emission of dibenzo-CDI **1** was fully recovered (Figure 3, the blue and black curves fully overlapped), thus indicating the dissociation of the dibenzo-CDI **1** 2 [K^+] complex.

Apart from the aggregation/disaggregation studies in solution, the thermotropic behavior and solid-state self-organization of dibenzo-CDI **1** were investigated as well. In the first step, the thermotropic behavior of dibenzo-CDI **1** was studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) (see Figure S19 in the Supporting Information and Figure 4 a,b). The DSC curves of dibenzo-CDI **1** showed two endothermic peaks upon heating, thus indicating a mesophase above 74 °C and an isotropic melt from 249 °C. The formation of the liquid crystalline phase was monitored by POM on an open film of dibenzo-CDI **1**, which was prepared by drop-casting from a 3 mg mL^{-1} chloroform solution. Slow cooling resulted in a dendritic texture, which is characteristic for a discotic columnar phase.[16] Apart from defect structures, the dendritic microstructure remains dark being in agreement with a homeotropic alignment of the columnar stacks towards the surface (Figure 4 a,b). Addition of K^+ or Pb^{2+} did not cause phase transitions. Interestingly, after complexation with K^+ or Pb^{2+}, these two complexes did not even melt within the investigated temperature range from 30 °C to 340 °C. This phenomenon is attributed to the immobilization of the crown ether subsitutents during metal ion binding.

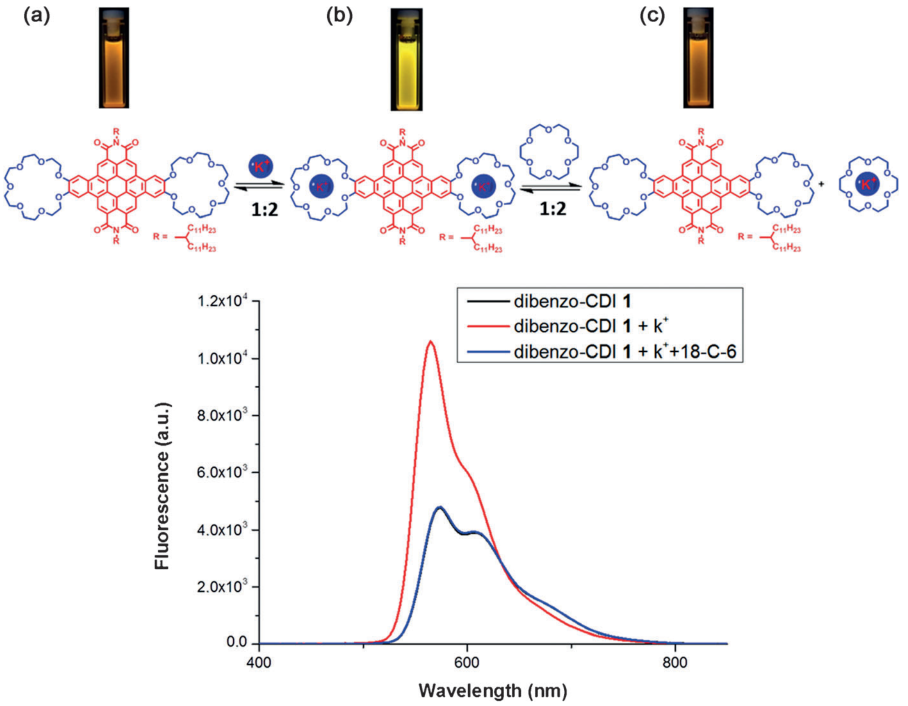

Figure 3. The inter-conversion of aggregation and disaggregation by external stimuli: fluorescence (100 μM in $CHCl_3/CH_3CN$ (1:1 v:v)) of (a) dibenzo-CDI **1** (100 μM); (b) dibenzo-CDI **1** (100 μM)+K^+ (200 μM); (c) dibenzo-CDI **1** (100 μM)+K^+ (200 μM)+18-crown-6 (200 μM).

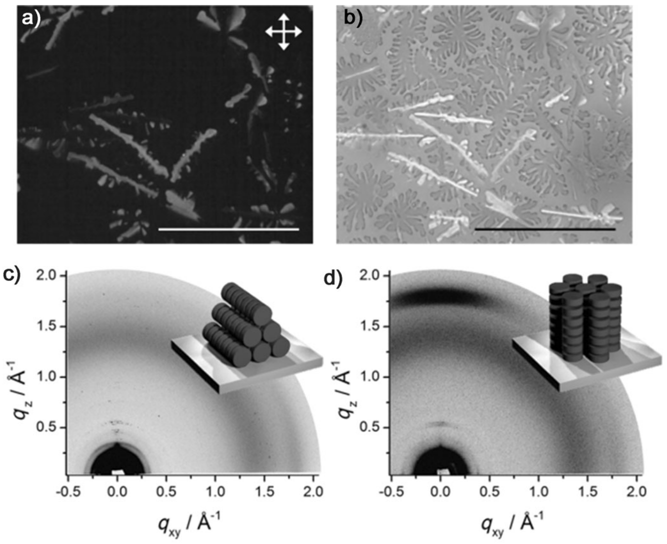

Figure 4. POM of dibenzo-CDI **1** film prepared by drop casting after cooling from the isotropic phase: a) with cross-polarizers (white arrows) and b) almost parallel polarizers (scale bar corresponds to 50 μm). GIWAXS of the dibenzo-CDI **1** film recorded at 30 °C: c) before and d) after annealing in the isotropic melt (insets illustrate the corresponding surface arrangement of **1**. The intercolumnar lattice is negleted).

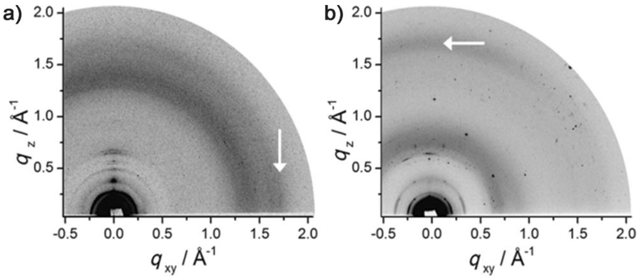

Figure 5. GIWAXS of dibenzo-CDI **1** film with a) K^+ and b) Pb^{2+} after solution depostion (white arrow indicates the π-stacking peak).

Next, grazing-incidence wide-angle X-ray scattering (GIWAXS) was used to understand the impact of metal ions on molecular organization on the surface. After solution deposition, dibenzo-CDI **1** organized in an edge-on fashion, whereby the columns were lying parallel to the surface. The π-stacking reflection was therefore located on the equatorial plane[17] of the GIWAXS pattern at $q_{x,y} = 1.80\ \text{Å}^{-1}$ corresponding to a real spacing of 3.5 Å (Figure 4c). In the stacks, the molecular discs were packed in an orthogonal manner, which is typical for a liquid crystalline columnar organization. Annealing of the isotropic melt resulted in a drastic reorganization of a face-on alignment as a consequence of the position change of the π-stacking reflection to the meridional plane of the pattern,[18] whereby the intracolumnar distance remained unchanged (Figure 4d). This homeotropic orientation, as determined by GIWAXS, is in agreement with the non-birefringent dendritic textures in the POM images of dibenzo-CDI **1** (Figure 4a, b). Additionally, the scattering intensities in the small-angle region imply a modification of the intercolumnar organization after annealing (see Figure S18a, b in the Supporting Information) from a rectangular unit cell with $a = 27.2$ Å and $b = 35.3$ Å to an oblique one with $a = 30.5$ Å, $b = 25.8$ Å and $\alpha = 65°$.

After direct solution deposition, dibenzo-CDI **1**+K^+ revealed slight differences in ordering as compared to the compound without metal ions (Figure 5a). The position of the π-stacking reflection on the equatorial plane proves an edge-on arrangement of the molecules, while the intermolecular distance within the stacks increased to 3.8 Å. The columnar organization changed as compared to the unmodified dibenzo-CDI **1** (see Figure S18c in the Supporting Information). In contrast to the addition of K^+, dibenzo-CDI **1**+Pb^{2+} organized face-on with a slightly decreased π-stacking distance of 3.7 Å, due to the smaller size of the lead ion (Figure 6). The enlarged packing space is related to the steric hindrance of the K^+ ions. Moreover, the structural data offer the possibility of controlling the surface organization of dibenzo-CDI **1** by annealing the isotropic phase or by applying metal ions of a defined size. Larger ions hinder the molecular interactions and lead to an edge-on arrangement in solution-processed films, while stronger aggregation provokes a face-on organization. A similar explanation can be applied to the change in the surface arrangement for parent dibenzo-CDI **1**. The molecular interactions are weaker in solution than in the isotropic melt because of the shorter molecular distances in the latter case.

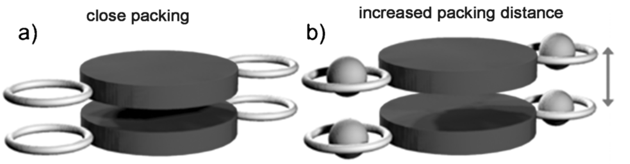

Figure 6. Illustration of the molecular packing of dibenzo-CDI **1** a) without and b) with metal ions.

In summary, we have presented the synthesis of the macrocyclic dibenzo-CDI **1** with two B21C7 moieties as a novel derivative of bay-extended PDIs. The introduction of B21C7 groups and alkyl swallow-tail substituents facilitates thermotropic liquid crystalline behavior. We demonstrated a facile host-guest supramolecular interaction to prevent the dibenzo-CDI **1** dye from aggregation in solution by forming a strong 1:2 complex with Pb^{2+} or K^+. Such a disaggregation process results in significant enhancement (37 % for Pb^{2+} and 31 % for K^+) of the fluorescence intensity. Thus dibenzo-CDI **1** can be used as a "turn-on" probe for Pb^{2+} or K^+. Furthermore, the size of the metal ions had a strong impact on the molecular packing and their surface organization, allowing a control between face-on and edge-on arrangement. This work will stimulate further research on covalently "decorating" flexible molecular recognition motifs onto rigid disc-shape molecules to build up new functional supramolecular π-conjugated systems.

Experimental Section

Synthetic procedures, material characterizations, and full details about the instrumentation can be found in the Supporting Information.

Acknowledgements

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Keywords: crown ether · dyes · sensors · supramolecular chemistry · surface organization

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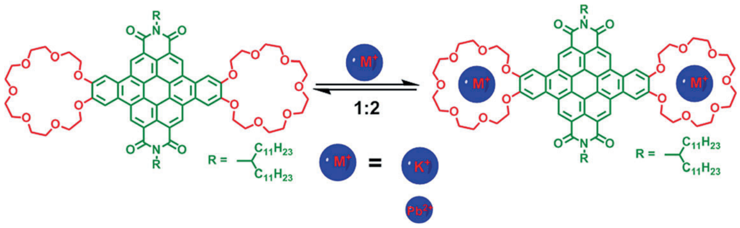
Supramolecular Sensors

Yingjie Ma, Tomasz Marszalek, Zhongyi Yuan, Rene Stangenberg, Wojciech Pisula, Long Chen, Klaus Müllen** ———— ▮▮▮▮–▮▮▮▮

VIP **A Crown Ether Decorated Dibenzocoronene Tetracarboxdiimide Chromophore: Synthesis, Sensing, and Self-Organization**



Sensing Sensibility: A macrocyclic dibenzocoronene tetracarboxdiimide containing two benzo-21-crown-7 groups has been synthesized. It shows liquid-crystalline behavior and selectively binds Pb^{2+} or K^{+} to form 1:2 complexes in solution. The complexation leads to a significant increase in fluorescence. The surface organization of discotic columnar structures, in the solid-state, can be controlled by selective ion binding.