Self-assembly and photoinduced electron transfer in a donor- β -cyclodextrin-acceptor supramolecular system[§]

RETHEESH KRISHNAN^{a,b}, SUMESH BABU KRISHNAN^{a,c}, BIJITHA BALAN^{a,d} and
KARICAL RAMAN GOPIDAS^{a,c,*}

^aPhotosciences and Photonics, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Council of Scientific and Industrial Research, Thiruvananthapuram 695 019, Kerala, India

^bPresent address: Department of Chemistry, Government College for Women, Thiruvananthapuram 695 014, Kerala, India

^cAcademy of Scientific and Innovative Research (AcSIR), New Delhi 110 001, India

^dPresent address: Department of Chemistry, Government College Kariavattom, Thiruvananthapuram 695 581, Kerala, India

E-mail: gopidaskr@rediffmail.com; gopidaskr@gmail.com

MS received 11 May 2018; accepted 1 August 2018; published online 17 September 2018

Abstract. Equimolar amounts of native β -cyclodextrin (β -CD), pyrene-linked adamantane (PYAD) and *tert*-butylpyromellitic diimide (PMDI) when dissolved in water self-assembled to form the supramolecular donor-acceptor system **PYAD**– β -CD–**PMDI**. The high affinity of adamantane derivatives for inclusion binding in the β -CD cavity and the propensity of PMDI to undergo rim-binding at the narrow rim of β -CD led to the formation of **PYAD**– β -CD–**PMDI**. The ternary complex **PYAD**– β -CD–**PMDI** was thoroughly characterized using various spectroscopic techniques. β -CD performs three functions in the self-assembled complex: (1) encapsulate the adamantane unit and keep the pyrene (PY) moiety above the secondary rim, (2) rim-bind PMDI and keep it at the primary rim, and (3) act as a spacer between pyrene and PMDI. Thus, the ternary complex can function as a donor-spacer-acceptor system capable of undergoing photoinduced electron transfer (PET). Upon excitation of the pyrene moiety in **PYAD**– β -CD–**PMDI** an electron is transferred from the excited pyrene to the PMDI ground state. Steady state and time resolved fluorescence experiments were carried out to study the PET in **PYAD**– β -CD–**PMDI**. Existence of the ternary system and PET processes taking place within it are further supported by laser flash photolysis experiments.

Keywords. Cyclodextrins; donor–acceptor systems; inclusion binding; PET; supramolecular assembly.

1. Introduction

Significant progress was made in the past decades in the design and study of supramolecular donor–acceptor (D–A) systems capable of undergoing photoinduced electron transfer (PET) reactions as models for natural photosynthetic reaction centers and artificial light harvesting systems.^{1–3} Hydrogen bonding, π -stacking and metal-ligand coordination are the most common interactions utilized in the design of non-covalent D–A systems.^{4–14} These interaction modes, however,

are not very useful in assembling D–A systems in aqueous solutions. Biological electron transfers occur in aqueous environments and in this context those interactions capable of achieving D–A assembly in aqueous solutions assume greater significance. Cyclodextrins (CDs), which are cyclic oligosaccharides with hydrophobic cavities, are ideal molecular receptors for building water-soluble supramolecular functional assemblies.^{15–19} Recently others^{20–29} and we^{30,31} have employed chromophore-appended CDs to assemble supramolecular D–A systems for PET reactions in

*For correspondence

[§]Dedicated to Professor M. V. George on the occasion of his 90th Birth Anniversary.

Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s12039-018-1535-z>) contains supplementary material, which is available to authorized users.

water. The hydrophobic nature of the CD cavity acts as the assembler of the D–A system here. This approach, however, suffers from the following disadvantages. In almost all the studies of PET reactions in CD based non-covalent systems the D (or A) component is covalently linked to the CD molecule and the ET partner is encapsulated into the CD cavity. Considerable time and effort are required for covalently linking organic chromophores on to CDs. Quite often, yields are low and mixtures are obtained. Since CDs have very low solubility in most organic solvents, chromatographic purification of CD-appended systems has to be performed in water. CDs and chromophore-appended CDs have similar polarity and hence column chromatography may have to be repeated several times to get small amounts of pure CD-linked systems. When chromophore-linked CDs are used as probes in PET reactions, presence of even very small amounts of native CD would lead to erroneous results because the guest molecule may get included into the native CD cavity in preference to the chromophore-appended CD cavity. Hence, development of alternate strategies for assembling supramolecular D–A systems that does not involve synthesis and purification of chromophore-appended CD appears very attractive.

Recently we have observed that *N*-alkyl derivatives of pyromellitic diimide (PMDI) can bind β -CD through the narrow rim and we have designated this mode of binding as ‘rim-binding’.³² In this mode of interaction the PMDI chromophore remains very close to the narrow rim with the *N*-alkyl substituent projected in to the β -CD cavity. We also showed that β -CD can simultaneously bind a PMDI derivative in the rim-binding mode and an adamantyl (AD) moiety through inclusion binding, thereby leading to the formation of ‘ternary complexes’.^{33,34} Using a variety of experimental techniques (UV-Vis spectroscopy, induced circular dichroism spectroscopy (ICD), cyclic voltammetry (CV), isothermal titration calorimetry (ITC), MALDI-TOF mass spectrometry and one and two dimensional NMR spectroscopy) we have confirmed the structures of rim-binding and ternary complexes. In this paper we tried to exploit the ability of β -CD to form ternary complexes to assemble a D- β -CD-A supramolecular system which is capable of undergoing PET up on excitation. In this design β -CD plays the role of an assembler and spacer (or bridge) between the D and A moieties.

2. Experimental

2.1 Materials and physical measurements

All the starting materials and reagents such as β -cyclodextrin, 1-pyrenecarboxaldehyde, 1-adamantylamine, pyromellitic

dianhydride, *tert*-butylamine, triphenylphosphine, tetrabromomethane and ethanolamine were purchased from Sigma Aldrich and used without further purification. All the solvents used for synthesis were from Merck and carefully dried using standard protocols. Water used was Millipore or double distilled. Synthesis and characterization of the molecules used in this study are given in the Supporting Information (SI), pages S3–S8.

The electronic absorption spectra were recorded using a Shimadzu UV-3101 UV-Vis NIR spectrophotometer. ITC data were obtained from microcal iTC 200. The raw data obtained were fitted and analysed using Origin 7.0 software provided along with the instrument. In all experiments the β -CD was taken in the cell and titrated using different PMDI solutions taken in the syringe. All NMR data were recorded in D₂O purchased from Aldrich, using a 500 MHz Bruker Avance DPX spectrometer. MALDI-TOF mass spectrometry was conducted on an AXIMA-CFR-plus instrument with 2,5-Dihydroxy benzoic acid as the matrix. Steady-state fluorescence experiments were performed with a SPEX Fluorolog F112X Spectrofluorimeter by using optically dilute solutions. The fluorescence spectra were corrected for the instrumental response. Dilute solutions having optical density 0.1 at the excitation wavelength (340 nm) were used for fluorescence quenching experiments. I_0/I plots were constructed using the fluorescence intensity at the emission maximum (375 nm). Time-resolved fluorescence experiments were performed by using an IBH picosecond single-photon counting system employing a 335 nm nano-LED excitation source and a Hamamatsu C4878-02 microchannel plate (MCP) detector. The laser flash photolysis experiments were performed using an Applied Photophysics Model LKS-60 laser kinetic spectrometer using the third harmonic (355 nm) from an INDI-40-10-HG Quanta Ray Nd-YAG laser.

3. Results and Discussion

PMDI derivatives are very good electron acceptors and these are frequently used as acceptors in PET reactions.^{35–43} We have employed pyrene (PY) as the donor in this study because PY has been employed as donor in several PET reactions.^{44–49} Our strategy for assembling the D- β -CD-A system which employed both the rim-binding and inclusion binding abilities of β -CD, is outlined in Scheme 1. Addition of *tert*-butylPMDI to an aqueous solution of native β -CD would result in the formation of the binary rim-binding complex (designated as β -CD>PMDI).^{33,34} When an AD derivative such as adamantylammonium chloride (ADAC) is added the ternary complex designated here as ADAC $\square$ β -CD>PMDI is formed.³³ If ADAC is replaced by pyrene-linked adamantane (PYAD), then the resulting ternary complex PYAD $\square$ β -CD>PMDI would have the structure shown in Scheme 1. In Scheme 1, the order of

Scheme 1. Strategy for self-assembling PMDI/β-CD/PYAD ternary system for PET.

addition shown is β-CD, PMDI, PYAD. We observed that the order of addition is immaterial and it is more convenient to add PMDI to pre-formed PYAD ⊃ β-CD. This is the approach followed in this paper.

Since PY is a good electron donor and PMDI is a good electron acceptor, the self-assembled ternary system PYAD ⊃ β-CD > PMDI is capable of undergoing PET reaction when PY moiety is excited. In this paper we report the self-assembly of the PYAD ⊃ β-CD > PMDI ternary complex and the PET process occurring in it up on excitation of PY. Native β-CD is used for the self-assembly and laborious functionalization of β-CD is avoided in the design.

3.1 Self-assembly of the ternary system PYAD ⊃ β-CD > PMDI

The ternary system was assembled from the constituents (1:1:1 molar ratio) in two steps. First, the binary inclusion complex PYAD ⊃ β-CD was assembled by adding one equivalent of PYAD to an aqueous solution of β-CD. One equivalent of PMDI was then added to get the ternary complex PYAD ⊃ β-CD > PMDI. Formation of the binary and ternary complexes was confirmed by several techniques. Our experiments have shown that the order of addition is immaterial. Identical ¹H NMR spectra were obtained for the ternary complex regardless of the order of addition.

3.2 Isothermal titration calorimetric studies

ITC experiments were carried out by taking β-CD (1 mM, 200 μL) in the cell and excess of PYAD (10 mM, 40 μL) in the syringe. Figure 1A shows the ITC titration curve for PYAD ⊃ β-CD formation. Heat changes observed for PYAD ⊃ β-CD system was adequate for fitting the data using the available software. Fit of the data gave values of $K_a = 3850 \pm 423 \text{ M}^{-1}$, $\Delta H = (-2.0238 \pm 0.081) \times 10^4 \text{ J mol}^{-1}$, $\Delta S = 8.12 \text{ J mol}^{-1} \text{ K}^{-1}$ and $n = 1.0$. The ITC data confirms 1:1 inclusion complex formation between PYAD and β-CD and the association constant obtained is very close to that reported for ADAC-β-CD interaction ($K_a = 8317 \pm 392 \text{ M}^{-1}$),^{50,51} indicating that the adamantane moiety in PYAD is included in the β-CD cavity in this complex. ΔS obtained from the fit was positive indicating that the binding process is not entirely enthalpy driven as observed for AD derivatives. In general, inclusion of a neutral molecule in the CD cavity proceeds with negative ΔS . When a charged molecule such as ADAC or PYAD is included, ΔS is usually positive due to 'dehydration of the organic guest'.^{52–54} PYAD is an amine salt and in aqueous solutions the NH_2^+ moiety would be surrounded by water dipoles. When the AD end of this molecule is included inside the β-CD cavity the water shell surrounding the NH_2^+ group is disrupted and this contributes towards the entropy increase. This factor becomes significant when the dehydrated group

Figure 1. The ITC data for titration of (A) β -CD against PYAD and (B) PYAD $\supset$ β -CD against PMDI.

is close to the moiety included in the cavity and will play a significant role in deciding the extent of penetration of the guest into the cavity.^{52–54} In fact it has been shown previously that compared to neutral adamantane derivatives ADAC penetrates the β -CD cavity only shallowly leaving some space in the CD cavity near the primary rim.^{55,56} A similar situation is expected when PYAD penetrates into the β -CD cavity. We expect the AD moiety of PYAD to penetrate shallowly into the β -CD cavity leaving some space near the narrow rim and in this configuration the PY moiety would remain above the wider rim in the aqueous environment. In other words, in the binary PYAD $\supset$ β -CD complex, the AD moiety is only partly included in the cavity and the PY moiety is placed above the wider rim and fully exposed to water.

Since K_a for the formation of PYAD $\supset$ β -CD is high, we expect a solution containing equimolar amounts of PYAD and β -CD to consist mostly of the binary complex. If PMDI is added to the above solution the ternary complex would be formed wherein the PMDI rim-binds to the PYAD $\supset$ β -CD by inserting the *tert*-butyl group into the cavity through the narrow rim. Since penetration of the AD group into the cavity is shallow, enough space would be available inside the cavity at the narrow rim for rim-binding. In order to ascertain the formation of the ternary complex, ITC experiment was performed with PYAD $\supset$ β -CD in the

cell and PMDI in the syringe. When the concentrations of PYAD $\supset$ β -CD and PMDI were 1.0 mM and 10 mM, respectively, the heat changes observed were low and the data could not be fitted. When the experiment was repeated with 1.5 mM PYAD $\supset$ β -CD and 15 mM PMDI, heat changes as shown in Figure 1B were obtained and the data could be fitted using available protocols. Fitting of the data gave $K_a = 1563 \pm 18.5 \text{ M}^{-1}$, $\Delta H = (-3.041 \pm 0.057) \times 10^4 \text{ J mol}^{-1}$, $\Delta S = -40.9 \text{ J mol}^{-1} \text{ K}^{-1}$ and $n = 0.85$. This experiment confirms the formation of PYAD $\supset$ β -CD $\supset$ PMDI from the binary complex PYAD $\supset$ β -CD and PMDI. It may be noted that K_a for ternary complexation is much less compared to that for binary complexation. The ternary complex formation proceeds with negative ΔS value, which also supports formation of a highly ordered system. In an earlier work we reported a ternary complex where we confirmed formation of the complex by induced circular dichroism (ICD) experiments also.³³ The ternary complex in that case exhibited negative ICD for the PMDI chromophore which could arise only if PMDI is rim-bound to β -CD.³³ Unfortunately, ICD experiments could not be carried out in the present case due to the very high extinction coefficients of the pyrene chromophore in the region of PMDI absorption. In this paper ternary complex formation is further confirmed by ^1H NMR and MALDI-TOF experiments.

Figure 2. ^1H NMR changes observed during addition of PMDI (0–1 eq.) to $\text{PYAD} \square \beta\text{-CD}$.

3.3 NMR titration studies

NMR titration experiments were carried out to investigate the structures of the binary and ternary complexes $\text{PYAD} \square \beta\text{-CD}$ and $\text{PYAD} \square \beta\text{-CD} > \text{PMDI}$. The AD moiety in PYAD exhibited three signals in the ^1H NMR: doublet of doublet (δ 1.70 – 1.83, 6H) for H_a , singlet (δ 2.20, 6H) for H_c and singlet (δ 2.26, 3H) for H_b (Figure S5, in Supplementary Information). Upon addition of 1 equivalent of $\beta\text{-CD}$ all the AD proton signals became broad and exhibited small downfield shifts (Figure S5) suggesting encapsulation of the AD part into the CD cavity. The aromatic protons of the PY moiety also exhibited some broadening suggesting that the pyrene residue is folded back so as to be near the wider rim of $\beta\text{-CD}$. (For the complete spectrum and structure of adamantyl group with protons marked see Figure S5 in Supplementary Information).

The ternary complex was assembled by adding one equivalent of PMDI to $\text{PYAD} \square \beta\text{-CD}$. Changes observed for the NMR signals during this addition are presented in Figure 2 (see Figure S6 (in Supplementary Information) for full spectra). It is evident from the figure that ^1H NMR signals of *tert*-butyl group of PMDI exhibited broadening with very small down-field shift of 0.05 ppm upon addition to $\text{PYAD} \square \beta\text{-CD}$. (This observation is in line with the earlier reported shift for PMDI protons when titrated against $\beta\text{-CD}$ ³³ (Figure S7 in

Supplementary Information)). The H_c proton of PYAD has become somewhat narrow and this is in line with the proposal of ternary complexation outlined in Scheme 1.

When the *tert*-butyl group of PMDI inserts through the narrow rim into the cavity, the AD moiety may be slightly pushed out. The H_c protons of AD which are placed away from the wider rim would move more into the aqueous environment resulting in a narrowing of its NMR signal. Aromatic protons of PMDI did not exhibit any change, but that of PYAD exhibited small changes as it is slightly pushed out into the aqueous environment as a result of PMDI rim-binding.

Presence of guest molecules within the CD cavity leads to considerable shifts in the ^1H NMR signals of $\beta\text{-CD}$ and these can be observed if the titration experiment is carried out in the reverse order. These studies would allow a better understanding of the location of the guest with respect to the various protons of $\beta\text{-CD}$ host. Such a study however requires unambiguous assignments of the chemical shifts of all $\beta\text{-CD}$ protons. Based on literature⁵⁷ and our own studies,^{33,34} ^1H NMR signals of $\beta\text{-CD}$ were unambiguously assigned as: H-1 - doublet at δ 5.94, H-2 - doublet of doublet at 3.64–3.66, H-3 - triplet at 3.97, H-4- triplet at 3.58, H-5 and H-6 - multiplet at 3.84–3.89 (Figure 3A). The H-3, H-5, one of the H-6 protons and the glycosidic O-4 oxygen are placed in the interior of the cavity. H-2, H-4 and one of the H-6 protons are on the outer wall of the $\beta\text{-CD}$. Locations

Figure 3. ^1H NMR spectra (zoomed-in image) of (A) β -CD, (B) β -CD + PYAD (1:1) and (C) β -CD + PYAD + PMDI (1:1:1). Concentrations of all components were 1.1×10^{-2} M. The lower panel also shows the position of various protons in β -CD. The protons inside the cavity are coloured red.

of the various protons in the CD cone are shown in the inset of Figure 3. When a guest is included in the cavity the H-3, H-5 and O-4 atoms will be affected. Since the O-4 is linked to C-4 which in turn is connected to H-4, the H-4 also would be affected. Thus, when a bulky guest is included through the wider rim ^1H NMR signals of H-3, H-5 and H-4 would be mainly affected, whereas rim-binding through the narrow rim would affect the H-5 and H-6 protons predominantly. It can be seen from Figure 3B that addition of PYAD to β -CD shifts the H-3 and H-5 protons considerably and the H-4 protons slightly. H-2 and H-6 protons were not affected. When one equivalent of PMDI was added to the above solution, the H-5 and H-6 proton signals move up-field (Figure 3C) and other proton signals remain unaffected. H-5 and H-6 protons are near the narrow rim and H-2 and H-3 are near the wider rim. The fact that H-5 and H-6 protons are affected by PMDI addition clearly indicates formation of the ternary complex by rim-binding of PMDI with PYAD $\square$ β -CD.

In a previous publication, we have probed the ternary complex ADAC $\square$ β -CD $\square$ PMDI (Scheme 1) using 2D ROESY NMR.³³ We observed cross-peaks between the adamantane protons and PMDI *tert*-butyl protons, suggesting that these protons are present in close proximity within the β -CD cavity. Because of the low solubility of PYAD, 2D ROESY experiments could not be performed for PYAD $\square$ β -CD $\square$ PMDI system. We do not expect

the PY moiety present outside the cavity to change the location of the groups within the cavity.

3.4 MALDI-TOF mass spectroscopic studies

In order to further confirm the formation of the binary complex PYAD $\square$ β -CD and ternary complex PYAD $\square$ β -CD $\square$ PMDI, MALDI-TOF mass spectroscopic studies were carried out. Figure S8A (Supplementary Information) shows the mass spectrum obtained for the binary complex PYAD $\square$ β -CD. The peak at 1501.35 corresponds to the mass of PYAD+ β -CD (without the counter ion Cl^-). The peak at 1524.60 corresponds to the mass of PYAD+ β -CD+Na. Figure S8B (Supplementary Information) shows the MALDI-TOF spectrum of ternary complex PYAD $\square$ β -CD $\square$ PMDI. The peak at 1879.60 corresponds to the mass of PYAD+ β -CD+PMDI (without counter anions). Similarly, the peaks at 1886.16, 1902.11 and 1919.03 correspond to PYAD+ β -CD+PMDI+Li, PYAD+ β -CD+PMDI+Na, and PYAD+ β -CD+PMDI+K, respectively. The MALDI-TOF data thus support formation of the binary and ternary complexes shown in Scheme 1.

3.5 Photophysical properties of PYAD, PYAD $\square$ β -CD and PYAD $\square$ β -CD $\square$ PMDI

Figure 4A presents the absorption spectra of PYAD in the absence and presence of β -CD. As can be seen from

Figure 4. Absorption spectrum of (A) PYAD (2.5×10^{-6} M) in the absence (red) and presence (blue) of β -CD (2.5×10^{-6} M) (B) PYAD (2.5×10^{-6} M), β -CD (2.5×10^{-6} M) complex with PMDI (2.5×10^{-6} M) added, and (C) Fluorescence spectrum of PYAD (2.5×10^{-6} M) in the absence (red trace) and presence (blue trace) of β -CD (2.5×10^{-6} M).

Figure 4A, absorption of the pyrene chromophore is unaffected when the AD moiety is included in the CD cavity, suggesting that the PY moiety is fully exposed to the aqueous environment in PYAD $\square$ β -CD. When one eq. of PMDI was added, the absorption spectrum changed to Figure 4B. Spectrum 4B is the sum of the absorptions due to PMDI and PYAD which suggested that there is no ground state interaction between the donor PY and acceptor PMDI chromophores in the ternary complex PYAD $\square$ β -CD $\triangleright$ PMDI.

Figure 4C shows the fluorescence spectra of PYAD in the absence and presence of β -CD which suggested that the fluorescence spectrum of PYAD is not affected upon inclusion in the CD cavity. Fluorescence lifetime of PYCD was also unaffected by encapsulation of the AD moiety in β -CD (vide infra). This further confirms that the PY moiety remains fully exposed to water in the binary complex. These experiments along with the ITC, and NMR data confirmed that the orientation of the pyrene moiety in the binary complexes is as shown in Scheme 1. The adamantane units are included in the β -CD cavity and the Pyrene moiety remains outside at the wider rim. When PMDI was added, it undergoes rim-binding with the binary complex leading to the formation of the ternary complex PYAD $\square$ β -CD $\triangleright$ PMDI.

3.6 Estimation of donor–acceptor distance in PYAD $\square$ β -CD $\triangleright$ PMDI

The donor-acceptor centre-to-centre distance (d_{cc}) is an important parameter in the study of PET reactions. In the ternary complex we proposed that the adamantane moiety is encapsulated into the β -CD cavity through the wider rim and the *tert*-butyl group of the PMDI is inserted into the cavity through the narrow rim of β -CD. We can make an estimate of d_{cc} if we assume that the *tert*-butyl group of PMDI and the ‘a’ or ‘b’ carbon atoms of AD are about 2 Å apart (Figure S9, Supplementary Information). The structures of PYAD and PMDI were

geometry optimized and d_{cc} was calculated assuming 2 Å separation between these moieties. The value thus obtained was ~ 15 Å. For the ensuing discussion of PET in the ternary system we assume that d_{cc} between the PMDI acceptor and Pyrene donor is ~ 15 Å (See Figure S9 in Supplementary Information for details).

3.7 Photoinduced electron transfer in the PYAD/ β -CD/PMDI system

Upon excitation of the pyrene chromophore in PYAD $\square$ β -CD $\triangleright$ PMDI an electron will be transferred from PY to PMDI as given in equation 1.

The free energy change ΔG^0 for the PET process can be calculated using the Weller equation,^{58,59}

$$\Delta G^0 = F(E_{\text{ox}} - E_{\text{red}}) - E_{00} - e^2 / \epsilon d_{cc} \quad (2)$$

where F is the faraday constant, E_{ox} is the oxidation potential of the donor, E_{red} the reduction potential of the acceptor, E_{00} is the excitation energy of the donor and ϵ is the dielectric constant of water. Using values of $E_{\text{ox}} = 1.16$ V, $E_{\text{red}} = -0.58$ V and $E_{00} = 3.34$ eV (from previous studies)^{30,31,60} we obtained $\Delta G^0 = -1.61$ eV, suggesting that ET from $^1\text{PY}^*$ to PMDI is thermodynamically feasible. The triplet energy (E_T) of pyrene is 2.1 eV. Substituting in equation 2, we can see that ET from $^3\text{PY}^*$ to PMDI is also feasible with $\Delta G^0 = -0.36$ eV. We have studied these PET processes using steady-state and time-resolved fluorescence measurements and also by laser flash photolysis.

3.8 Steady state fluorescence quenching experiments

Fluorescence spectrum of the binary complex PYAD $\square$ β -CD (2.5×10^{-5} M each in PYAD and β -CD) is shown in Figure 5a. Upon addition of increasing amounts of PMDI the fluorescence intensity of the binary complex

Figure 5. Fluorescence spectra of PYAD $\square$ β -CD (2.5×10^{-5} M) in the absence (a) and presence (b-g) of PMDI. The concentrations of PMDI was varied between 6.25×10^{-5} M to 3.12×10^{-4} M. Inset shows the I_0/I plot for the quenching. Excitation wavelength was 350 nm.

decreased as shown in Figure 5b–g. Fluorescence quenching can occur by energy transfer or electron transfer mechanisms. In the present case energy transfer cannot occur because the singlet energy of PMDI is higher than that of pyrene (Absorption spectrum of PMDI is given in Figure S10 in Supplementary Information). Since ΔG^0 for PET is negative, the quenching must be due to PET from $^1\text{PY}^*$ to PMDI.

In an aqueous solution containing PYAD, β -CD and PMDI, the binary complex and ternary complex would co-exist with the constituent molecules as shown in Scheme 2. Photo excitation of PY would lead to static and dynamic PET processes shown in Scheme 2. Since the association constants for PYAD with β -CD is very high, we assume that in an aqueous solution containing equimolar amounts of PYAD and β -CD, most of the molecules would exist as the binary complex PYAD $\square$ β -CD. When PMDI molecules are added to the above solution, a part of the PMDI molecules undergo rim binding with the binary complex PYAD $\square$ β -CD to form the ternary complex PYAD $\square$ β -CD $\gg$ PMDI. Within the ternary complex the donor and acceptor moieties are placed at a distance of ~ 15 Å to facilitate electron transfer from the donor to the acceptor. This constitutes the unimolecular (or static) electron transfer pathway. The unbound PMDI molecule can freely diffuse and accept an electron from $^1\text{PY}^*$ or $^1\text{PY}^*\text{AD}\beta\text{-CD}$. These constitute the diffusion mediated (or dynamic) ET pathways (Scheme 2). The Stern-Völmer plot constructed from the quenching data showed an upward curvature (Figure 5 inset) which indicates that both static and dynamic quenching processes are taking place in the system. In order to confirm this, quenching of PY by PMDI was performed in acetonitrile where only the dynamic component can exist. The fluorescence quenching and Stern-Völmer plots for the same are

Scheme 2. Self-assembly and quenching processes in PYAD/ β -CD/PMDI system.

Figure 6. Fluorescence decay profiles of PYAD $\square$ β -CD (1:1, 2.5×10^{-6} M), in the (a) absence and (b–d) presence of PMDI (1.0 to 2.5×10^{-3} M); e is lamp profile.

given in Figure S11 in Supplementary Information. The Stern–Völmer plot was linear suggesting the presence of only dynamic quenching in this solvent. From the slope (K_{SV}) of Figure S11 B the quenching rate constant obtained was $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is very close to the diffusion controlled value in this solvent.

3.9 Time-resolved fluorescence experiments

The two quenching pathways (unimolecular and diffusion mediated) were further confirmed using time resolved fluorescence experiments. PYAD in aqueous solution exhibited mono-exponential decay with lifetime of $\tau_0 = 126 \text{ ns}$. Upon addition of β -CD the binary complex PYAD $\square$ β -CD is formed which also exhibited single exponential decay with the same lifetime. When PMDI was added to this solution the nature of decay changed to bi-exponential, with two lifetime values. The decay profiles of the binary complex PYAD $\square$ β -CD in the absence and presence of different PMDI concentrations are shown in Figure 6.

Scheme 2 shows the various quenching processes that can occur in the PYCD/ β -CD/PMDI system. As per the scheme both static and dynamic quenching pathways exist and this leads to the observed bi-exponential decay profiles.^{8,30,31,35,61} The bi-exponential profiles were fitted using equation 3 to obtain lifetimes τ_1 and τ_2 and their respective contributions χ_1 and χ_2 .

$$I_t = \chi_1 \exp(-t/\tau_1) + \chi_2 \exp(-t/\tau_2) \quad (3)$$

Lifetime τ_1 is actually the fluorescence lifetime of the ternary complex PYAD $\square$ β -CD $\square$ PMDI. Compared to the fluorescence lifetime of PYAD ($= \tau_0$) value of τ_1 will be low because of the unimolecular or static quenching of fluorescence within the ternary complex by PET. It can be shown that^{30,31,35,61,62}

$$\tau_1 = (k_0 + k_{et})^{-1} \quad (4)$$

where k_{et} is the rate of unimolecular electron transfer within PYAD $\square$ β -CD $\square$ PMDI and $k_0 = 1/\tau_0$. Lifetime τ_2 results from the diffusion mediated electron transfer pathways. In Scheme 2, two diffusional quenching pathways are identified, namely, quenching of free PYAD by PMDI (rate constant k_1) and quenching of the binary complex PYAD $\square$ β -CD by free PMDI (rate constant k_2). Since PYAD and PYAD $\square$ β -CD exhibited same fluorescence spectrum and fluorescence lifetime, the total diffusion mediated quenching rate $k_1[\text{PMDI}] + k_2[\text{PMDI}]$ is taken as equal to $k_q[\text{PMDI}]$, where $k_q = k_1 + k_2$. Under this condition, the lifetime τ_2 is defined by equation 5.^{30,31,61}

$$\tau_2 = (k_0 + k_q[\text{PMDI}])^{-1} \quad (5)$$

All fit parameters obtained including τ_1 and τ_2 for the lifetime quenching are provided in the SI (Table ST1 in Supplementary Information). For all the fits χ^2 values were in the range of 1–1.2 and weighted residuals were randomly distributed around zero. As per equations 3 and 4, τ_1 should be independent of PMDI concentration and τ_2 values depend on PMDI concentration. Values of τ_1 and τ_2 obtained were plotted against [PMDI] in Figures S12 A, B (in Supplementary Information) and these plots confirm that values of τ_1 and τ_2 meet the above conditions. Inspection of Table ST1 in Supplementary Information shows that for entry 5, values of τ_1 and τ_2 are similar. In order to confirm the reliability of the fit parameters the data were refitted by assuming a constant value of $\tau_1 = 84 \text{ ns}$. The fit parameters obtained from this analysis are given in Table ST2 (Supplementary Information). The fit parameters in both tables are very similar, thus confirming the reliability of the analysis.

Since $k_0 = 1/\tau_0$, equations 4 and 5 can be rearranged to give equations 6 and 7, respectively.

$$k_{et} = 1/\tau_1 - 1/\tau_0 \quad (6)$$

$$\tau_0/\tau_2 = 1 + k_q\tau_0[\text{PMDI}] \quad (7)$$

From equation 6 we obtained $k_{et} = 3.97 \times 10^6 \text{ s}^{-1}$ using the average value of $\tau_1 = 84 \text{ ns}$. The diffusion mediated quenching rate constant k_q can be obtained by plotting τ_0/τ_2 vs [PMDI] as per equation 7. The slope of this plot is equal to $k_q\tau_0$. Plot of τ_0/τ_2 vs [PMDI] is shown in Figure 7. k_q value obtained from this plot is $1.65 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The diffusion rate constant k_{diff} in water = $7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁶³ The k_q value obtained is lower than k_{diff} due to the large size of the molecules involved and the presence of similar charges on the fluorophore and quencher.

Figure 7. Plot of τ_0 / τ_2 vs [PMDI].

As mentioned above, we obtained $k_{et} = 3.97 \times 10^6 \text{ s}^{-1}$ for electron transfer from PY to PMDI within the ensemble PYAD $\square$ β -CD>PMDI. In order to see if this value of k_{et} is meaningful, we have analysed the PET process in PYAD $\square$ β -CD>PMDI using Marcus theory. The details are included in the SI (section 9, Pages S17–18 in Supplementary Information). Using experimental/literature values of ΔG^0 and reorganization energies λ_s and λ_v , we calculated the donor-acceptor coupling elements H_{el} and H_{cl}^0 and the damping factor (also known as distance decay constant) β . The β value obtained is 1.2 and this value is characteristic of systems where electron transfer occurs through-space in a hydrophobic media.

3.10 Laser flash photolysis experiments

Laser flash photolysis of PYAD $\square$ β -CD was carried out using the 3rd harmonic of a Nd-YAG laser and the spectrum obtained along with kinetic traces are shown in Figure S13 (in Supplementary Information). The spectrum exhibited absorption bands at 420 and

460 nm, which are assigned respectively to the T_1 - T_n and S_1 - S_n absorptions of pyrene. Transient spectrum of PY in organic solvents were reported earlier^{64,65} and the spectrum in Figure S13 (Supplementary Information) closely matched with the reported spectra. This confirms that the aqueous environment, the attached AD moiety and presence of β -CD did not influence the excited state properties of PY. Transient absorption spectrum of PYAD $\square$ β -CD recorded in the presence of PMDI ($2.5 \times 10^{-4} \text{ M}$, 5 eq.) is shown in Figure 8. The spectrum showed a very sharp peak at 460 nm and weak absorptions in the 650–740 nm region.

In order to assign the peaks to possible transient intermediates we have carried out several control experiments. Transient absorption of the above system in the presence of oxygen is shown in Figure S14 (Supplementary Information). It can be seen in Figure S14 that the absorption profile in the 650–800 nm disappears in the presence of oxygen. Both radical anions and triplets are highly sensitive to oxygen. Since the 460 nm peak is insensitive to oxygen we assign this to $PY^{\bullet+}$ formed as a result of PET as per equation 1. $PY^{\bullet+}$ is known to absorb in the 440–460 nm region. The absorption in the 650–800 nm region in Figure 8 is assigned to $PMDI^{\bullet-}$ based on its similarity to reported $PMDI^{\bullet-}$ spectrum⁶⁶ and also its sensitivity to oxygen. It can be noticed that both the S_1 - S_n and T_1 - T_n absorptions (observed in Figure S13, Supplementary Information) are absent in Figure 8, suggesting that electron transfer has occurred from both the singlet and triplet excited states of pyrene to the ground state of PMDI.

Although we have assigned the 460 nm peak in Figure 8 to $PY^{\bullet+}$ and the 720 nm peak to $PMDI^{\bullet-}$, further control experiments were required to confirm this assignment. For example, if PET had occurred as per equation 1, then $PY^{\bullet+}$ and $PMDI^{\bullet-}$ must be formed in

Figure 8. Transient absorption spectrum of PYAD $\square$ β -CD/PMDI (1:1:5) system. Inserts show the kinetic traces at 460 and 720 nm.

Scheme 3. Protonation of $\text{PMDI}^{\bullet-}$ by water.

equal amounts. Reported extinction coefficient values of $\text{PY}^{\bullet+}$ ($11,400 \text{ M}^{-1} \text{ cm}^{-1}$ in D_2O)^{67,68} and $\text{PMDI}^{\bullet-}$ ($41,700 \text{ M}^{-1} \text{ cm}^{-1}$ in DMF)⁶⁶ suggest that 420 nm : 720 nm peak intensity ratio should be $\sim 1:4$ if PET has occurred as per equation 1. The observed intensity ratio in Figure 8 is 1:0.5, which suggest that the observed concentration of $\text{PMDI}^{\bullet-}$ is only $1/8^{\text{th}}$ of the expected value.

We propose that the intensity of the $\text{PMDI}^{\bullet-}$ peak is very low because of its protonation reaction with water. It is well known that radical anions are protonated in protic solvents.^{68,69–70} Protonation of $\text{PMDI}^{\bullet-}$ can occur as shown in Scheme 3.

Most radicals will have absorption at wavelengths below 400 nm and hence the protonated species was not observed in the flash photolysis experiment. In order to confirm this proposal, we have carried out the following control experiments.

A mixture of pyrene and PMDI in acetonitrile (1:5) was flash photolyzed and the spectrum obtained is shown in Figure S15 (Supplementary Information). The 460 nm peak is due to $\text{PY}^{\bullet+}$ and the 720 nm peak is assigned to $\text{PMDI}^{\bullet-}$. The intensity ratio of these peaks is $\sim 1:6$ in Figure S15 and this number is in good agreement with the reported extinction coefficients ($\text{PY}^{\bullet+}$ in ACN^{67,68} = $5,100 \text{ M}^{-1} \text{ cm}^{-1}$ and $\text{PMDI}^{\bullet-}$ in DMF = $41,700 \text{ M}^{-1} \text{ cm}^{-1}$).⁶⁶ The transient species $\text{PY}^{\bullet+}$ and $\text{PMDI}^{\bullet-}$ decay by BET. The decay of $\text{PMDI}^{\bullet-}$ at 720 nm was analysed using second order kinetics to give BET rate constant $k = 2.73 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (see Figure S16 in Supplementary Information). Since Figure S16 gave a good linear fit, one can safely assume that complete decay of the transients occurs by BET. Thus, in ACN solution the PET process occurred as given in equation 1.

We observed that addition of water has a profound effect on the intensities of the $\text{PY}^{\bullet+}$ and $\text{PMDI}^{\bullet-}$ absorptions. Figure S17 (in Supplementary Information) shows the transient absorption spectrum of the above PY/PMDI (1:5) system in ACN/Water (2:1). Compared to Figure S15, the peak intensity ratio has changed much. Presence of water led to an increase in the intensity of the $\text{PY}^{\bullet+}$ absorption and drastic decrease in the $\text{PMDI}^{\bullet-}$ absorption. Examination of the kinetic traces at 720 nm in the absence and presence of water suggested that decrease in the $\text{PMDI}^{\bullet-}$ peak intensity is

due to static quenching by water (Figure S17, inset). In a 2:1 ACN/water system the PMDI molecules may have few water molecules close to it. Some of the $\text{PMDI}^{\bullet-}$ formed will be immediately protonated as shown in Scheme 3 which account for the drastic decrease in the intensity of the 720 nm peak in the presence of water. This hypothesis was further confirmed by flash photolysis of the PYAD/PMDI system in 100% water in the absence of β -CD. The transient absorption spectrum obtained is shown in Figure S18 (in Supplementary Information). The 420 nm peak of $\text{PY}^{\bullet+}$ is very intense indicating that PET has occurred but the 720 nm peak was absent indicating that all of $\text{PMDI}^{\bullet-}$ formed was protonated by water as shown in Scheme 3.

Because of the protonation reaction $\text{PMDI}^{\bullet-}$ is not stable in water and it will not be possible to obtain its extinction coefficient in water. Assuming the extinction coefficient in DMF for $\text{PMDI}^{\bullet-}$ and using the known extinction coefficient of $\text{PY}^{\bullet+}$ in water one can calculate the actual concentrations of $[\text{PY}^{\bullet+}]$ and $[\text{PMDI}^{\bullet-}]$ formed in the flash photolysis of PYAD/ β -CD/PMDI (1:1:5) system from Figure 8. The values obtained are $[\text{PY}^{\bullet+}] = 1.45 \times 10^{-5} \text{ M}$ and $[\text{PMDI}^{\bullet-}] = 1.97 \times 10^{-6} \text{ M}$. Thus, the concentration of $\text{PMDI}^{\bullet-}$ is only about 13% of that of $\text{PY}^{\bullet+}$. We propose that the 13% of $\text{PMDI}^{\bullet-}$ that survives the protonation reaction corresponds to the fraction of PMDI engaged in ternary complex $\text{PYAD} \square \beta\text{-CD} \triangleright \text{PMDI}$ formation (Scheme 2). In the ternary complex the alkyl group-linked end of PMDI is slightly inserted into the narrow rim of β -CD and hence protected from water molecules. This suggests that the concentration of the ternary complex in Scheme 2 is about 13% of PYAD concentration. The laser flash photolysis experiments thus lend further support for the formation of the ternary complex $\text{PYAD} \square \beta\text{-CD} \triangleright \text{PMDI}$ and PET taking place within it.

We mentioned that only 13% of $\text{PY}^{\bullet+}/\text{PMDI}^{\bullet-}$ formed in the irradiation of the PYAD/ β -CD/PMDI system can undergo BET and the remaining ion radicals must undergo decay by other pathways. Decay pathways of $\text{PY}^{\bullet+}$ are well investigated in the literature.^{67,71–73} The most common decay pathway is its reaction with ground state PY to give a dimer radical cation $(\text{PY-PY})^{\bullet+}$ which exhibits absorption near 800 nm and $> 1300 \text{ nm}$ in water.

Both these ion radicals react with anions. The decay mechanism in the absence of any such species, as in the present case, is not very certain. In the present case formation and decay of the dimer radical cation is evident from the small absorptions seen in the region >700 nm in Figure S18 (in Supplementary Information). The decay of this transient is much slower compared to decay of $\text{PY}^{\bullet+}$ at 460 nm (see inset of S18). Regarding the decay of $\text{PMDI}^{\bullet}$, no reports are available in the literature. The most probable decay pathways for radicals are (1) radical-radical coupling and radical addition to unsaturated systems. Product analysis would be required for complete understanding of the decay pathways of $\text{PMDI}^{\bullet}$ in the present case. We may undertake this work in the future.

4. Conclusions

We have assembled a non-covalent donor-acceptor system in aqueous solution with the aid of β -CD. The donor is adamantane-linked pyrene and the acceptor is *N*-tert-butylpyromellitic diimide. When equimolar amounts of the donor, acceptor and β -CD were dissolved in water, a ternary complex is formed where the β -CD simultaneously binds both PYAD and PMDI. The PYAD is held at the wider rim through inclusion binding and the PMDI is held at the narrow rim through rim-binding interaction. The self-assembly of the components into the ternary system is confirmed by ITC, NMR, and MALDI-TOF studies. The self-assembled ternary system is capable of undergoing photoinduced electron transfer. Steady state and time resolved fluorescence experiments confirm photoinduced electron transfer taking place from pyrene to PMDI moiety in the ternary complex. The rate constant for the intra-complex electron transfer was determined from fluorescence lifetime studies. Further evidence for the PET reaction taking place in the ternary system is obtained from laser flash photolysis studies.

Supplementary Information (SI)

Synthesis details, ^1H and ^{13}C NMR, MALDI and other experimental details are included in supporting information. The SI also contains a Marcus theory analysis of the obtained PET rate. Supplementary Information is available at www.ias.ac.in/chemsci.

Acknowledgements

The authors thank DAE-BRNS (No. 2007/37/37/BRNS), and CSIR for financial support. R.K. and S. B. K. are grateful to CSIR for fellowships. This is contribution number NIIST-PPG 348.

References

- Bottari G, Trukhina O, Ince M and Torres T 2012 Towards Artificial Photosynthesis: Supramolecular Donor-Acceptor Porphyrin and Phthalocyanine/Carbon Nanostructure Ensembles *Coord. Chem. Rev.* **256** 2453
- D'Souza F and Ito O 2009 Supramolecular Donor – Acceptor Hybrids of Porphyrins/Phthalocyanines with Fullerenes/Carbon Nanotubes: Electron Transfer Sensing, Switching, and Catalytic Applications *Chem. Commun.* 4913
- Hasobe T, Fukuzumi S and Kamat P V 2006 Hierarchical Assembly of Porphyrins and Fullerenes for Solar Cells *Interface* **15** 47
- Das A, Jha A, Gera R and Dasgupta J 2015 Photoinduced Charge Transfer State Probes the Dynamic Water Interactions with Metal – Organic Nanocages *J. Phys. Chem. C* **119** 21234
- Das A and Ghosh S 2014 Supramolecular Assemblies by Charge – Transfer Interactions between Donor and Acceptor Chromophores *Angew. Chem. Int. Ed.* **53** 2038
- D'Souza F, Amin A, N, El-Kouhly M E, Subbaiyan N K, Zandler M E and Fukuzumi S 2012 Control over Photoinduced Energy and Electron Transfer in Supramolecular Polyads of Covalently linked azaBODIPY-Bisporphyrin 'Molecular Clip' Hosting Fullerene *J. Am. Chem. Soc.* **134** 654
- Bikram C K C, Subbaiyan N K and D'Souza F 2012 Supramolecular Donor – Acceptor Assembly Derived from Tetracarbazole – Zinc Phthalocyanine Coordinated to Fullerene: Design, Synthesis, Photochemical, and Photoelectrochemical Studies *J. Phys. Chem. C* **116** 11964
- Takai A, Chkounda M, Eggenspieler A, Gros C P, Lachkar M, Barbe J-M and Fukuzumi S 2010 Efficient Photoinduced Electron Transfer in a Porphyrin Tripod-Fullerene Supramolecular Complex via π - π interactions in Nonpolar Media *J. Am. Chem. Soc.* **132** 4477
- Honda T, Nakanishi T, Ohkubo K, Kojima T and Fukuzumi S 2010 Structure and Photoinduced Electron Transfer Dynamics of a Series of Hydrogen-Bonded Supramolecular Complexes Composed of Electron Donors and a Saddle-Distorted Diprotonated Porphyrin *J. Am. Chem. Soc.* **132** 10155
- Gayathri S S, Wielopolski M, Perez E M, Fernandez G, Sanchez L, Viruela R, Orti E, Guldi D M and Martin N 2009 Discrete Supramolecular Donor-Acceptor Complexes *Angew. Chem. Int. Ed.* **48** 815
- Kira A, Umeyama T, Matano Y, Yoshida K, Isoda S, Park J K, Kim D and Imahori H 2009 Supramolecular Donor-Acceptor Heterojunctions by Vertical Stepwise Assembly of Porphyrins and Coordination-Bonded Fullerene Arrays for Photocurrent Generation *J. Am. Chem. Soc.* **131** 3198
- Kuramochi Y, Satake A, Itou M, Ogawa K, Araki Y, Ito O and Kobuke Y 2008 Light-Harvesting Supramolecular Porphyrin Macrocycle Accommodating a Fullerene-Tripodal Ligand *Chem. Eur. J.* **14** 2827
- Wang Y B and Lin Z Y 2003 Supramolecular Interactions between Fullerenes and Porphyrins *J. Am. Chem. Soc.* **125** 6072

14. D'Souza F, Deviprasad G R, Zandler M E, Hoang V T, Klykov A, VanStipdonk M, Perera A, El-Khouly M E, Fujitsuka M and Ito O 2002 Spectroscopic, Electrochemical, and Photochemical Studies of Self-Assembled via Axial Coordination Zinc Porphyrin-Fulleropyrrolidine Dyads *J. Phys. Chem. A* **106** 3243
15. Crini G A 2014 History of Cyclodextrin *Chem. Rev.* **114** 10940
16. Chen G and Jiang M 2011 Cyclodextrin – Based Inclusion Complexation Bridging Supramolecular Chemistry and Macromolecular Self-Assembly *Chem. Soc. Rev.* **40** 2254
17. Rekharsky M V and Inoue Y 1998 Complexation Thermodynamics of Cyclodextrins *Chem. Rev.* **98** 1875
18. Al-Burtomani S K S and Suliman F O 2018 Experimental and theoretical study of the inclusion complexes of epinephrine with β -cyclodextrin, 18-crown-6 and cucurbit[7]uril *New J. Chem.* **42** 5785
19. Al-Dubaili N, El-Tarabily, K and Saleh N 2018 Host-guest complexes of imazalil with cucurbit[8]uril and β -cyclodextrin and their effect on plant pathogenic fungi *Sci. Rep.* **8** 2839
20. Li H, Li F, Zhang B, Zhou X, Yu F and Sun L 2015 Visible Light – Driven Water Oxidation Promoted by Host – Guest Interaction between Photosensitizer and Catalyst with a High Quantum Efficiency *J. Am. Chem. Soc.* **137** 4332
21. Dryza V and Bieske E J 2015 Electron Injection and Energy Transfer Properties of Spiropyran – Cyclodextrin Complexes Coated onto Metal Oxide Nanoparticles: Toward Photochromic Light Harvesting *J. Phys. Chem. C* **119** 14076
22. Zhang Y-M, Chen Y, Zhuang R-J and Liu Y 2011 Supramolecular Architectures of Tetrathiafulvalene – bridged Bis (β – cyclodextrin) with Porphyrin and its Electron Transfer Behaviors *Photochem. Photobiol. Sci.* **10** 1393
23. Fukuhara G, Mori T and Inoue Y 2009 Competitive Enantiodifferentiating Anti-Markovnikov Photoaddition of Water and Methanol to 1,1 – Diphenylpropene Using A Sensitizing Cyclodextrin Host *J. Org. Chem.* **74** 6714
24. Freeman R, Finder T, Bahshi L and Willner I 2009 β – Cyclodextrin – Modified CdSe/ZnS Quantum Dots for Sensing and Chiroselective Analysis *Nano. Lett.* **9** 2073
25. Liang P, Zhang H-Y, Yu Z-L and Liu Y 2008 Solvent – Controlled Photoinduced – Electron Transfer between Porphyrin and Carbon Nanotubes *J. Org. Chem.* **73** 2163
26. Ghosh S, Mondal S K, Sahu K and Bhattacharyya K 2006 Ultrafast Electron Transfer in a Nanocavity. Dimethylaniline to Coumarin Dyes in Hydroxypropyl - γ - Cyclodextrin *J. Phys. Chem. A* **110** 13139
27. Deng W, Onji T, Yamaguchi H, Ikeda N and Harada A 2006 Competitive Photoinduced Electron Transfer by the Complex Formation of Porphyrin with Cyclodextrin bearing Viologen *Chem. Commun.* **40** 4212
28. Wang Y-H, Zhu M-Z, Ding X-Y, Ye J-P, Liu L and Guo Q-X 2003 Photoinduced Electron Transfer between Mono-6-p-nitrobenzoyl- β -Cyclodextrin and Adamantanamine-Cn-porphyrins *J. Phys. Chem. B* **107** 14087
29. Haider J M, Williams R. M, De Cola L and Pikramenou Z 2003 Vectorial Control of Energy-Transfer Processes in Metallocyclodextrin Heterometallic Assemblies *Angew. Chem. Int. Ed.* **42** 1830
30. Balan B and Gopidas K R 2007 An Anthracene-Appended β -Cyclodextrin-Based Dyad: Study of Self- Assembly and Photoinduced Electron-Transfer Processes *Chem. Eur. J.* **13** 5173
31. Balan B and Gopidas K R 2006 Photoinduced Electron Transfer in α -Cyclodextrin-Based Supramolecular Dyads: A Free-Energy-Dependence Study *Chem. Eur. J.* **12** 6701
32. Balan B, Sivadas D L and Gopidas K R 2007 Interaction of Pyromellitic Diimide Derivatives with β -Cyclodextrin and Anthracene-Appended Beta-Cyclodextrin: Rim-binding vs Inclusion Complexation *Org. Lett.* **9** 2709
33. Krishnan R, Rakhi A M and Gopidas K R 2012 β Cyclodextrin-Pyromellitic Diimide Complexation. Conformational Analysis of Binary and Ternary Complex Structures by Induced Circular Dichroism and 2D NMR Spectroscopies *J. Phys. Chem. C* **116** 25004
34. Krishnan R and Gopidas K R 2011 β -Cyclodextrin as an End to End Connector *J. Phys. Chem. Lett.* **2** 2094
35. Kola S, Kim J H, Ireland R, Yeh M-L, Smith K, Guo W and Katz H E 2013 Pyromellitic Diimide – Ethylene-based Homopolymer Film as an N-Channel Organic Field-Effect Transistor Semiconductor *ACS Macro. Lett.* **2** 664
36. Guo X and Watson M D 2011 Pyromellitic Diimide-Based Donor – Acceptor Poly(phenyleneethynylene)s *Macromolecules* **44** 6711
37. Zheng Q, Huang J, Sarjeant A and Katz H E 2008 Pyromellitic Diimides: Minimal Cores for High Mobility n-Channel Transistor Semiconductors *J. Am. Chem. Soc.* **130** 14410
38. Lockard J E and Wasielewski M R 2007 Intramolecular Electron Transfer within a Covalent, Fixed-Distance Donor-Acceptor Molecule in an Ionic Liquid *J. Phys. Chem. B* **111** 11638
39. Lukas A S, Zhao Y, Miller S E and Wasielewski M R 2002 Biomimetic Electron Transfer using Low Energy Excited States: A Green Perylene-Based Analogue of Chlorophyll a *J. Phys. Chem. B* **106** 1299
40. Lukas E S, Miller S E and Wasielewski M R 2000 Femtosecond Optical Switching of Electron Transport Direction in Branched Donor-Acceptor Arrays *J. Phys. Chem. B* **104** 931
41. Sessler J L, Brown C T, O'Connor D, Springs S L, Wang R, Sathiosatham M and Hirose T 1998 A Rigid Chlorin-Naphthalene Diimide Conjugate. A Possible New Noncovalent Electron Transfer Model System *J. Org. Chem.* **63** 7370
42. Wiederrecht G P, Niemczyk M P, Svec W A and Wasielewski M R 1996 Ultrafast Photoinduced Electron Transfer in a Chlorophyll-Based Triad: Vibrationally Hot Ion Pair Intermediates and Dynamic Solvent Effects *J. Am. Chem. Soc.* **118** 81
43. Lee O P, Yiu A T, Beaujuge P M, Woo C H, Holcombe T W, Millstone J E, Douglas J D, Chen M S and Fréchet J M J 2011 Efficient Small Molecule Bulk Heterojunction Solar Cells with High Fill Factors via Pyrene-Directed Molecular Self-Assembly *Adv. Mater.* **23** 5359

44. Maligaspe E, Sandanayaka A S D, Hasobe T, Ito O and D'Souza F 2010 Sensitive Efficiency of Photoinduced Electron Transfer to Band Gaps of Semiconductive Single-Walled Carbon Nanotubes with Supramolecularly Attached Zinc Porphyrin Bearing Pyrene Glues *J. Am. Chem. Soc.* **132** 8158
45. Anh N V, Schlosser F, Groeneveld M M, van Stokkum I H M, Wurthner F and Williams R M 2009 Photoinduced Interactions in a Pyrene-Calix[4]arene-Perylene Bisimide Dye System: Probing Ground-State Conformations with Excited-State Dynamics of Charge Separation and Recombination *J. Phys. Chem. C* **113** 18358
46. Narita M, Mima S, Ogawa N and Hamada F 2001 Fluorescent Molecular Sensory System Based on Bis Pyrene-Modified γ -Cyclodextrin Dimer for Steroids and Endocrine Disruptors *Anal. Sci.* **17** 379
47. Murakami H, Hohsaka T, Asshizuka Y and Sisido M 1998 Site-Directed Incorporation of p-Nitrophenylalanine into Streptavidin and Site-to-Site Photoinduced Electron Transfer from a Pyrenyl Group to a Nitrophenyl Group on the Protein Framework *J. Am. Chem. Soc.* **120** 7520
48. Ueno A, Suzuki I and Osa T 1989 Association Dimers, Excimers, and Inclusion Complexes of Pyrene-Appended γ -Cyclodextrins *J. Am. Chem. Soc.* **111** 6391
49. Gelb R I, Schwartz L M and Laufer D A 1984 Adamantan-1-ylamine and Adamantan-1-ylamine Hydrochloride Complexes with Cycloamyloses *J. Chem. Soc., Perkin Trans. 2* 15
50. Briggner L-E, Ni X -R, Tempesti F and Wadsö I 1986 Microcalorimetric Titration of β -Cyclodextrin with Adamantane-1-Carboxylate *Thermochim. Acta* **109** 139
51. Hallén D, Schön A, Shehatta I and Wadsö I 1992 Microcalorimetric Titration of α -Cyclodextrin with some Straight-chain Alkan-1-ols at 288.15, 298.15 and 308.15 K *J. Chem. Soc., Faraday Trans.* **88** 2859
52. Rekharsky M V, Mayhew M P, Goldberg R N, Ross P D, Yamashoji Y and Inoue Y 1997 Thermodynamic and Nuclear Magnetic Resonance Study of the Reactions of α - and β -Cyclodextrin with Acids, Aliphatic Amines, and Cyclic Alcohols *J. Phys. Chem. B* **101** 87
53. Ross P D and Rekharsky M V 1996 Thermodynamics of Hydrogen Bond and Hydrophobic Interactions in Cyclodextrin Complexes *Biophys. J.* **71** 2144
54. Breslow R, Czamiecki M F, Emert J and Hamaguchi H 1980 Improved Acylation Rates within Cyclodextrin Complexes from Flexible Capping of Cyclodextrin and from Adjustment of Substrate Geometry *J. Am. Chem. Soc.* **102** 762
55. Emert J and Breslow R 1975 Modification of Cavity of Beta-Cyclodextrin by Flexible Capping *J. Am. Chem. Soc.* **97** 670
56. Schneider H J, Hacket F and Rudiger V 1998 NMR Studies of Cyclodextrin and Cyclodextrin Complexes *Chem. Rev.* **98** 1755
57. Rehm D and Weller A 1970 Kinetics of Fluorescence Quenching by Electron and H-atom Transfer *Isr. J. Chem.* **8** 259
58. Rehm D and Weller A 1969 Thermodynamics of the Formation of Excited EDA (electron donor-acceptor) Complexes *Ber. Bunsenges. Phys. Chem.* **73** 834
59. Fagnoni M, Mella M and Albini A 1998 Electron-Transfer-Photosensitized Conjugate Alkylation *J. Org. Chem.* **63** 4026
60. de Rege P J F, Williams S A and Therien M J 1995 Direct Evaluation of Electronic Coupling Mediated by Hydrogen Bonds: Implications for Biological Electron Transfer *Science* **269** 1409
61. Turro N J, Ramamurthy V and Scaiano J C *Principles of Molecular Photochemistry: An Introduction* (Sausalito, California: University Science Books) p. 471
62. Sessler J L, Wang B and Harriman A 1993 Long-range Photoinduced Electron Transfer in an Associated but Non-Covalently linked Photosynthetic Model System *J. Am. Chem. Soc.* **115** 10418
63. Pérez-Prieto J, Pérez L P, González-Béjar M, Mirandab M A and Stiriba S-E 2005 Pyrene-Benzoylthiophene Bichromophores as Selective Triplet Photosensitizers *Chem. Commun.* 5569
64. Raytchev M, Pandurski E, Buchvarov I, Modrakowski C and Fiebig T 2003 Bichromophoric Interactions and Time-Dependent Excited State Mixing in Pyrene Derivatives. A Femtosecond Broad-Band Pump-Probe Study *J. Phys. Chem. A* **107** 4592
65. Rak S F, Jozefiak T H and Miller L L 1990 Electrochemistry and Near-Infrared Spectra of Anion Radicals Containing Several Imide or Quinone Groups *J. Org. Chem.* **55** 4794
66. Hara M, Tojo S, Kawai K and Majima T 2004 Formation and Decay of Pyrene Radical Cation and Pyrene Dimer Radical Cation in the Absence and Presence of Cycodextrins during Resonant Two-Photon Ionization of Pyrene and Sodium 1-Pyrene Sulfonate *Phys. Chem. Chem. Phys.* **6** 3215
67. Naqvi K R and Melø T B 2006 Reduction of Tetranitromethane by Electronically Excited Aromatics in Acetonitrile: Spectra and Molar Absorption Coefficients of Radical Cations of Anthracene, Phenanthrene and Pyrene *Chem. Phys. Lett.* **428** 83
68. Cho D W, Fujitaska M, Yoon U C and Majima T 2008 Intermolecular Photoinduced Electron Transfer of 1,8-Naphthalimides in Protic Polar Solvents *Phys. Chem. Chem. Phys.* **10** 4393
69. Parker V D, Tilset M and Hammerich O 1987 Aromatic Hydrocarbon Dianions: Super Bases. Anthracene Anion Radical and Dianion Conjugate Acid PKa values *J. Am. Chem. Soc.* **109** 7906
70. Funston A M, Lyman S V, Price B S, Czapski G and Miller J R 2007 Rate and Driving Force for Protonation of Aryl Radical Anions in Ethanol *J. Phys. Chem. B* **111** 6895
71. Kira A, Arai S and Imamura M. 1971 Pyrene Dimer Cation as Studies by Pulse Radiolysis *J. Chem. Phys.* **34** 4890
72. Rodgers M A J 1972 Nanosecond pulse radiolysis of acetone. Kinetic and thermodynamic properties of some aromatic radical cations *J. Chem. Soc. Faraday Trans. 1* **68** 1278
73. Mori Y, Shinoda H, Nakano T and Kitagawa T 2002 Formation and Decay Behaviors of Laser-Induced Transient Species from Pyrene Derivatives 1. Spectral Discrimination and Decay Mechanisms in Aqueous Solution *J. Phys. Chem. A* **106** 11743