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Light harvesting vesicular donor–acceptor scaffold limits the rate of charge recombination in the presence of an electron donor†

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Rijo T. Cheriya, Ajith R. Mallia and Mahesh Hariharan*

We report the synthesis and excited state properties of a single component light harvesting donor–acceptor dyad (*R/S*)-NP(OH)₂ containing an α,β -dihydroxypropyl side-chain that can undergo molecule–bilayer–vesicle–gel–crystal transition. By virtue of steric hindrance offered by orthogonal naphthalimide and 2,6-diisopropylphenyl substituents, very weak H-type excitonic interactions between the perylenimide units resulted in high fluorescence quantum yield in the dyad-based metastable vesicular gel having a near-quantitative excitation energy transfer from naphthalimide to perylenimide. Femtosecond transient absorption measurements of the dyad (*R/S*)-NP(OH)₂: indole co-gel show that the vesicular scaffold promoted extension of the survival time of charge separated states (~1.4 ns) when compared to ultrafast charge recombination (~6 ps) in dyad (*R/S*)-NP(OH)₂: indole solution.

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Broader context

Energy as well as electron transfer processes in self-assembled systems are crucial in the development of artificial light harvesting and solar cell based functional materials. Existing non-covalent donor–acceptor containing self-assembled light harvesting systems lack control of: (i) stoichiometry; (ii) orientation; and (iii) distance; between the constituent donor and acceptor units that can limit the efficiency of excitation energy transfer. We choose a perylenimide–naphthalimide chromophoric array for the present study, known to be a potential and stable material in photonic devices. Our present findings offer efficient excitation energy transfer in covalently linked donor–acceptor dyads in a self-assembled vesicular gel and photoinduced electron transfer properties in the presence of an external electron donor (indole) doped co-gel that could help in the design of artificial light harvesting/photonic devices with improved energy and charge transport properties.

Introduction

Excitation energy and electron transfer processes in crowded environments are vital for natural^{1–4} and artificial^{5–7} photosynthesis and photonic applications.^{8–12} Such processes in isolated donor–acceptor (D–A) systems still attract immense interest.¹³ Non-covalent D–A pairs that exhibit efficient light harvesting and favourable excited-state properties in condensed media such as the amorphous, thin film,¹⁴ vesicle,^{15–18} gel,^{19–22} liquid crystal²³ and crystalline²⁴ states have received recent attention. Despite being efficient in light-harvesting and colour-tunable properties,^{19–21,25} the major limitations of D–A co-assemblies are the control²⁶ of: (i) stoichiometry; (ii) distance; and (iii) orientation; between the donor and the acceptor units. Excitation energy transfer in self-assembled covalent D–A dyads, which

includes the amorphous,²⁷ thin film,^{28,29} crystal^{27,30,31} and liquid crystalline states³² has received less attention. The dearth of literature reports on light harvesting self-assembled covalent D–A dyads could be due to the strong propensity of the aromatic surface³³ to self-assemble^{34,35} and subsequent exciton interactions^{36–38} or electron transfer^{39–42} that could alter the excited state properties. By virtue of their curvature properties,⁴³ vesicular scaffolds^{44,45} could be superior for light harvesting processes similar to the chromatophoric vesicular assembly in the natural photosynthetic unit.⁴⁶ A single molecular D–A dyad that can assemble to form a vesicle-gel and retain favourable excited state properties could be a potential scaffold for light harvesting applications. Concurrently, Wasielewski and co-workers have pioneered covalent D–A pairs that can undergo photoinduced electron transfer in aggregates, extending the lifetime of the charge-separated intermediates.^{42,47,48} However, the combination of light harvesting and charge separation in self-assembled architectures has received limited attention.^{41,49} We demonstrate that vesicular scaffold of a covalent D–A antenna can harvest light efficiently and can undergo photo-induced energy followed by electron transfer in the presence of an electron donor.

School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, CET Campus, Sreekaryam, Thiruvananthapuram, Kerala, INDIA 695 016. E-mail: mahesh@iisertvm.ac.in

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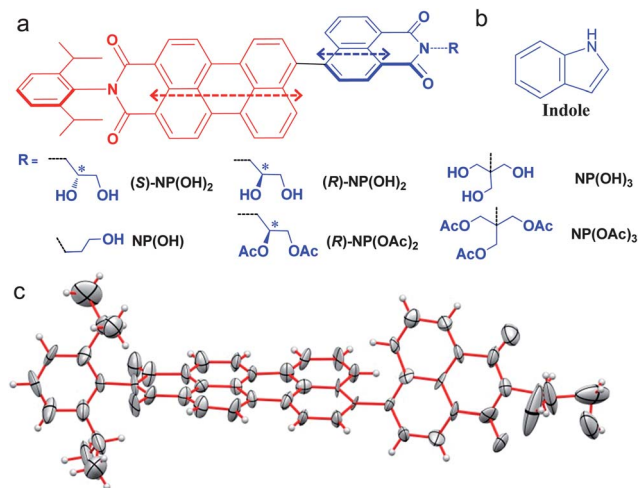


Fig. 1 Chemical structure of the molecules under investigation and the crystal structure of the dyad (R) -NP(OH)₂. Molecular structure of (a) the dyads NP(OH), (R/S) -NP(OH)₂, (R) -NP(OAc)₂, NP(OH)₃, NP(OAc)₃, arrows indicate the orientation of the transition dipole moment of the naphthalimide (NI) and perylenimide (PI) units; (b) indole (electron donor) and (c) single crystal X-ray structure of the dyad (R) -NP(OH)₂ (See CIF).

We recently reported efficient excitation energy transfer in the near-orthogonal naphthalimide (donor)–peryleneimide (acceptor) dyad NP(OH) in both the solution and crystalline state (Fig. 1).^{31,50} A subtle modification of the dyad using an (R/S) - α,β -dihydroxypropyl side-chain imparted optimal amphiphilicity to promote the formation of a (R/S) -NP(OH)₂ based vesicular gel in a 1 : 2 dichloromethane (DCM)–hexane mixture that allowed us to investigate the photoinduced processes of the covalent D–A pair in the gel state. To the best of our knowledge, this is the first report of a covalent D–A vesicle–gel that possesses efficient ‘Forster-type’ light harvesting properties resulting in orange–red fluorescence ($\lambda_{em} = 584$ nm) and high-fluorescent quantum yield ($\Phi_f = 54\%$). The vesicular gel of (R/S) -NP(OH)₂ exhibits stability in the presence of an electron donor (indole) making the dyad-donor co-gel, a potential candidate for combining efficient light harvesting and charge separation properties.

Results

The dyads (R/S) -NP(OH)₂ were synthesised through Stille coupling between a tributyltin derivative of perylenimide and 4-bromo- N -(R/S)-2,3-dihydroxypropyl naphthalimide (Scheme S1†).^{50,51} Monohydroxy NP(OH),^{50,51} trihydroxy NP(OH)₃ and protected analogues NP(OAc)₂ and NP(OAc)₃ of the dyad, having different degrees of amphiphilicity, were also synthesised (Scheme S1 and S2†). The UV-Vis absorbance of dyad (R) -NP(OH)₂ (Fig. 2a) in DCM could be described as the sum of the absorbance of naphthalimide (NI) centred at 340 nm and perylenimide (PI) centred at 480 nm, indicating that (R) -NP(OH)₂ behaves as individual chromophores although connected by a covalent bond (Fig. S1†). X-Ray structure (Fig. 1c), cyclic voltammetry and photophysical studies of the dyad (R) -

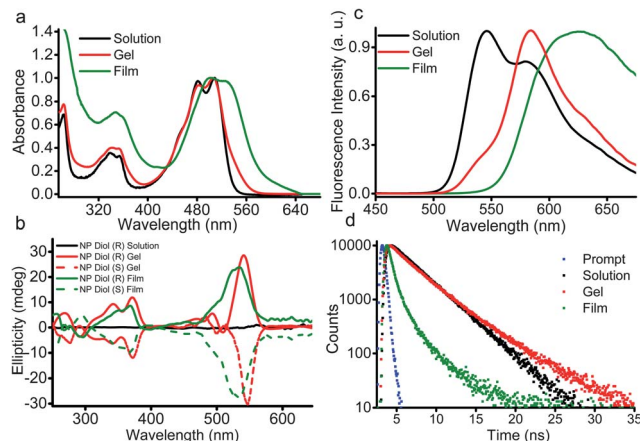


Fig. 2 Light harvesting and chiroptical properties of dyad NP(OH)₂ in the solution, gel and film state. (a) UV-Vis absorption spectra; (b) CD spectra; (c) fluorescence spectra ($\lambda_{ex} = 345$ nm) and (d) time-resolved fluorescence decay of (R) -NP(OH)₂ in DCM [black], (R) -NP(OH)₂ gel in a DCM–hexane (1 : 2) mixture [red], (R) -NP(OH)₂ thin film [green] and prompt [blue] when excited at 340 nm and emission collected at 550 nm (solution) and 580 nm (gel and film). (S) -NP(OH)₂ gel [dashed red] and thin film [dashed green] only for CD spectra.

NP(OH)₂ and structurally analogous NP(OH)⁵⁰ indicated near-orthogonal arrangement and negligible orbital interactions between the constituent naphthalimide and perylenimide units. The absence of a circular dichroism (CD) signal (Fig. 2b) corresponding to NI/PI units indicates the presence of equal amounts of mutually enantiomeric atropisomers^{52,53} of the (R/S) -NP(OH)₂ in DCM (Fig. S2†), consistent with both the axially chiral forms (1 : 1) in the unit cell. Upon direct excitation of the PI unit at 475 nm, (R) -NP(OH)₂ in DCM exhibited fluorescence emission ($\Phi_f = 0.75 \pm 0.04$) centred at 546 nm, with a shoulder at 580 nm corresponding to the PI unit (Fig. S3†). Upon excitation at 345 nm, efficient energy transfer⁵⁴ from the singlet excited state of NI to the PI unit of (R) -NP(OH)₂ in DCM resulted in PI emission centred at 546 nm (Fig. 2c). Time-resolved fluorescence of (R) -NP(OH)₂ in DCM exhibited mono-exponential decay with a lifetime of 3.7 ns, when excited at 340 nm (Fig. 2d) and 439 nm (Fig. S4a and b†). Increasing volume fraction of hexane in a solution of (R) -NP(OH)₂ in DCM showed a blue-shift of 5 nm and a systematic decrease in the UV-Vis absorbance centred at 513 nm with the formation of a band around 560 nm (Fig. S5†). Upon excitation at 345 nm, the observed significant quenching and blue-shift in the PI emission of (R) -NP(OH)₂ at lower DCM–hexane ratio could be attributed to H-type perylenimide aggregates in (R) -NP(OH)₂. Orthogonally arranged steric groups such as (i) diisopropylphenyl and (ii) NI units on either side could prevent stronger association of PI units in (R) -NP(OH)₂.

¹HNMR titration of (R) -NP(OH)₂ in CD₂Cl₂ with increase in volume fraction of hexane (0–67%) shows significant upfield shift and broadening in the protons corresponding to the NI and PI units (Fig. S6†) which indicates hydrophobic interactions between aromatic units that result in the self-assembly of (R) -NP(OH)₂ in a DCM–hexane mixture. A critical (R) -NP(OH)₂ concentration of 1 mM in a DCM–hexane (1 : 2) mixture offered

a stable red transparent gel. The d -spacing at 3.7 Å in the (*R*)-NP(OH)₂ xerogel is indicative of the interplanar distance between two adjacent PI units through π - π interactions, as is evident from powder X-ray diffraction (XRD; Fig. S7†). The broad XRD peaks show clearly a less-ordered intermolecular close packing arrangement in the gel compared to the sharp peaks observed in the non-gelated powdered (*R*)-NP(OH)₂ solid.⁵⁵ Infrared absorption spectra exhibited red-shifted broad peaks at 3432 cm⁻¹ (sol-gel) and 3446 cm⁻¹ (xerogel) when compared to the sharp peak at 3545 cm⁻¹ in the non-gelated solid (*R*)-NP(OH)₂ suggesting intermolecular hydrogen-bonding interactions (Fig. S8†). Similar results were obtained for the (*S*)-NP(OH)₂ isomer of the dyad. However, NP(OH), NP(OH)₃, NP(OAc)₂ and NP(OAc)₃ could not gelate under similar conditions, implying the role of amphiphilicity and/or chirality imparted by the hydroxypropyl side-chain in (*R/S*)-NP(OH)₂ in the formation of the gel. Moreover, (*R/S*)-NP(OH)₂ in DCM showed negligible self-aggregation even up to 0.8 mM (*R/S*)-NP(OH)₂, as understood from UV-Vis absorbance data (Fig. S5c and d†) indicating the role of the DCM-hexane mixture in the formation of the dyad based vesicular gel.

Dynamic light scattering (DLS) experiments suggest the formation of spherical particles having an average hydrodynamic diameter of 65 nm and a polydispersity index of 0.17 for 0.01 mM freshly prepared (*R*)-NP(OH)₂ in a DCM-hexane (1 : 2) solution (Fig. 3a and S9a†). With an increase in the concentration of (*R*)-NP(OH)₂ (0.01–0.25 mM), a progressive increase in

the average diameter of the particles, ranging from 65–190 nm, indicates the concentration-dependent size distribution of the spherical aggregates (Fig. 3a–e). Over the passage of time (~15 min), we observed an initial (*R*)-NP(OH)₂ concentration-dependent increase in the diameter (Fig. S9b†). This reveals the aggregation of smaller particles leading to the formation of a gel at the critical concentration of 1 mM (*R*)-NP(OH)₂. Initial rate kinetic analysis of the increase in particle size offered a first-order rate constant of $k = 0.03 \text{ min}^{-1}$ with respect to the dyad for 0.01 mM (*R*)-NP(OH)₂ (Fig. S10†). At 0.25 mM (*R*)-NP(OH)₂, we observed a first-order rate constant $k = 0.09 \text{ min}^{-1}$ implying that the rate of particle size growth enhances with an increase in the initial concentration of (*R*)-NP(OH)₂.

Atomic force microscopy (AFM) images at different initial concentrations of (*R*)-NP(OH)₂ were recorded. At 0.05 mM (*R*)-NP(OH)₂, we observed a distribution of spherical particles having an average diameter of 60 nm (Fig. S11a†), consistent with the DLS data (Fig. 3f). As the initial concentration of (*R*)-NP(OH)₂ increased to 0.1 mM, we observed the coalescence of spherical particles to form a linear (Fig. 3g) assembly that gels at a higher concentration (Fig. 3h). The scanning electron microscopy (SEM) image of 0.1 mM (*R*)-NP(OH)₂ confirms the formation of regular spherical particles having an average diameter of 160 nm (Fig. 3i and S11b†). As the concentration increases from 0.01 mM to 0.5 mM (*R*)-NP(OH)₂, SEM showed the fusion of spherical particles leading to the formation of a coalesced assembly of spherical aggregates, consistent with the

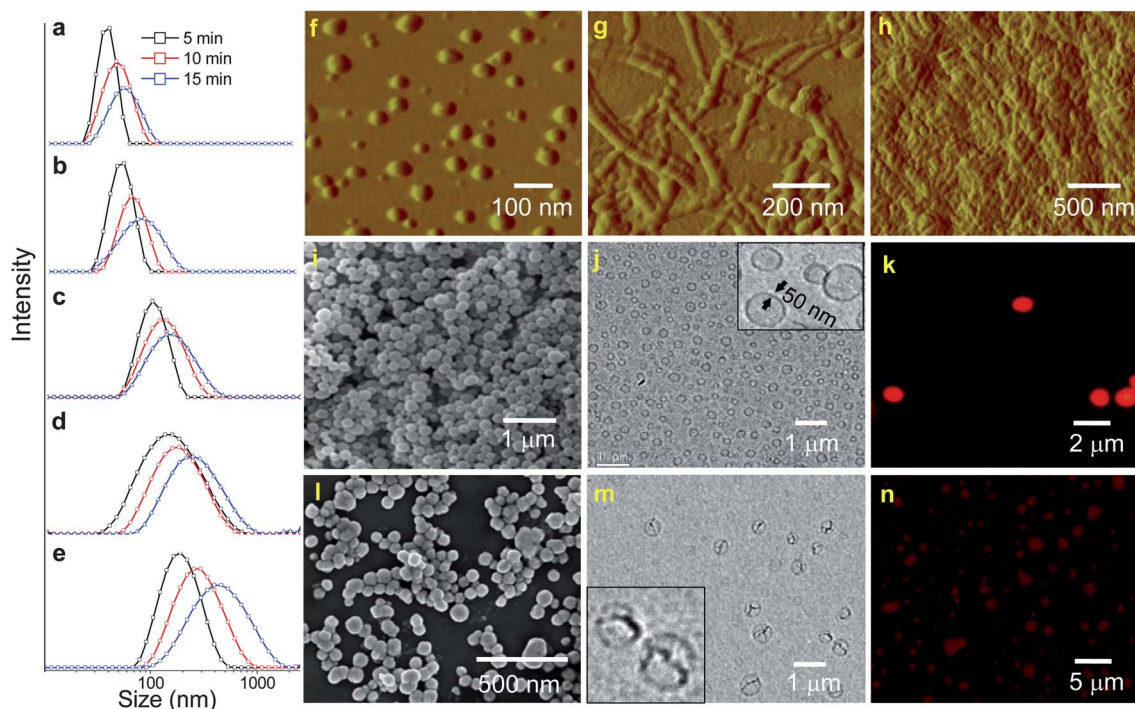


Fig. 3 Dynamic light scattering and microscopic investigation of the vesicular scaffold. Time-dependent size distribution of spherical aggregates at: (a) 0.01; (b) 0.02; (c) 0.05; (d) 0.1; and (e) 0.25 mM (*R*)-NP(OH)₂ in DCM-hexane (1 : 2) determined by DLS measurements. Tapping mode AFM images of (*R*)-NP(OH)₂ at: (f) 0.05; (g) 0.1; and (h) 0.5 mM (amplitude image Z scale = 12.9 (f), 45.8 (g) and 103.1 (h) mV respectively). SEM images of 0.1 mM (*R*)-NP(OH)₂ in the (i) absence and (l) presence of indole (1 mM). HR-TEM images of 0.25 mM (*R*)-NP(OH)₂ in the (j) absence and (m) presence of indole (2.5 mM). OM images ($\lambda_{\text{ex}} = 365 \text{ nm}$) of 0.25 mM (*R*)-NP(OH)₂ in the (k) absence and (n) presence of indole (2.5 mM) in a DCM-hexane (1 : 2) mixture.

AFM data (Fig. S12a–f†). The transmission electron microscopy (TEM) image of 0.25 mM (*R*)-NP(OH)₂ exhibited an average diameter of 260 nm of spherical particles (Fig. 3j and S11c†). The observed contrast between the periphery (*ca.* 50 nm thickness) and the inner part indicate the vesicular nature of the spherical particles. Under similar conditions, bright fluorescent red spheres with an average diameter of 650 nm were visible in the optical microscope (OM) when excited at 365 nm (Fig. 3k).

UV-Vis absorption spectrum of (*R*)-NP(OH)₂ gel exhibited absorbance at 341 nm (NI) and 505 nm (PI) having a shoulder at 550 nm (Fig. 2a) corresponding to weak PI aggregates. (*R*)-NP(OH)₂ thin film exhibited significantly red-shifted (~21 nm) absorbance at 530 nm (PI) indicating the presence of strong PI aggregates. The (*R*)-NP(OH)₂ gel exhibited strong positively induced CD signals at 370 nm and 545 nm corresponding to NI and PI units, similar to the (*R*)-NP(OH)₂ thin film (Fig. 2b). Negatively induced CD signals were obtained for the (*S*)-NP(OH)₂ gel and the thin film corresponding to NI and PI units. A strong red–orange fluorescence ($\Phi_f = 0.54 \pm 0.02$; $\lambda_{em} = 584$ nm) is exhibited by the (*R*)-NP(OH)₂ gel when excited both at 345 nm and 475 nm (Fig. 2c and S3†). The observed spectral narrowing (fwhm = 60 nm) in the emission of (*R*)-NP(OH)₂ gel compared to the thin film (fwhm = 130 nm) could be attributed to the re-absorption of photons due to a high optical density in the gel state. Upon excitation both at 345 nm and 475 nm, the thin film of (*R*)-NP(OH)₂ exhibited a significantly red-shifted ($\lambda_{em} = 625$ nm), weak, broad fluorescence corresponding to PI ($\Phi_f = 0.05 \pm 0.002$), consistent with the UV-Vis absorption data.

Picosecond time-resolved fluorescence of (*R*)-NP(OH)₂ gel (Fig. 2d) exhibited a bi-exponential decay, having lifetimes of 2.9 ns (53%) and 4.7 ns (47%) upon excitation at 340 nm. Similar lifetimes were observed on exciting the perylenimide unit at 439 nm (Fig. S4c and d†). The relatively minor component could be attributed to the slower decay of excimeric PI in the dyad (*R*)-NP(OH)₂ gel, while the short-lived component could be attributed to the monomeric PI. (*R*)-NP(OH)₂ in DCM exhibited a moderately faster rate of radiative decay ($k_r = 1.9 \times 10^8$ s⁻¹) compared to gel ($k_r = 1.4 \times 10^8$ s⁻¹; see ESI†) which indicates that the PI units undergo very weak H-type exciton interactions in the (*R*)-NP(OH)₂ gel, consistent with high-fluorescence quantum yield. (*R*)-NP(OH)₂ thin films showed tri-exponential decay, having lifetimes of 3.9 ns (11%), 1.2 ns (34%) and 0.3 ns (55%) upon excitation at 439 nm (Fig. S4e and f†), consistent with the recently reported literature.⁵⁶ Tri-exponential and faster radiative decay ($k_r = 0.37 \times 10^8$ s⁻¹) of the (*R*)-NP(OH)₂ thin film compared to solution indicates diverse close packing arrangements of PI aggregates that possess strong H-type exciton interactions resulting in the low Φ_f in thin film.³¹

Time-resolved fluorescence anisotropy of the dyad (*R*)-NP(OH)₂ gel exhibits an initial anisotropy value of 0.17 that loses the anisotropic memory when monitored at 580 nm (PI moiety) with a decay time of 201 ps, upon excitation at 439 nm (PI unit; Fig. S13†). Ultrafast energy/exciton migration^{57,58} at a short separation between the chromophoric transition dipoles predominates over slower fluorescence depolarization through rotational motion at this time-scale in the gel, leading to

fluorescence anisotropy.^{59,60} A relatively slower rate of energy migration ($k_{EM} = 4.97 \times 10^9$ s⁻¹; $\lambda_{ex} = 439$ nm) for the (*R*)-NP(OH)₂ gel compared to chromophoric gel assemblies²⁰ could be attributed to the delayed memory loss arising from the asymmetry of bichromophoric (*R*)-NP(OH)₂.

Temperature-dependent UV-Vis absorbance of the (*R*)-NP(OH)₂ gel exhibited a hypochromism at 550 nm and a concomitant increase in the absorbance at 505 nm (Fig. S14a†) which indicates the dissociation of exciton interactions between the PI units at elevated temperature resulting in the destabilisation of the gel ($T_m = 35$ °C). With an increase in temperature (20–60 °C), the (*R/S*)-NP(OH)₂ gel shows a gradual decrease in the intensity of CD signal at 370 nm and 545 nm (Fig. S15†). Disappearance of the NI and PI CD signals at elevated temperature indicates destabilisation of the gel through thermal unstacking of NI and PI units. Upon excitation at 345 nm and 475 nm, we observed a recovery in the fluorescence quantum yield of (*R*)-NP(OH)₂ ($\Phi_f = 0.65 \pm 0.03$) at 60 °C (Fig. S14b and c†) corresponding to the monomeric (*R*)-NP(OH)₂. Temperature-dependent time-resolved fluorescence decay of an (*R*)-NP(OH)₂ gel corresponding to the PI unit, upon excitation at 340 nm, exhibited a transformation of bi-exponential decay at 20 °C to mono-exponential decay at 60 °C ($\tau = 3.8$ ns). The mono-exponential decay of (*R*)-NP(OH)₂ gel at elevated temperature is consistent with the formation of monomeric (*R*)-NP(OH)₂ and the disappearance of the self-assembled structure (Fig. S14d†).

Amphiphilic (*R*)-NP(OH)₂ in a DCM–hexane mixture at a low concentration forms individual multi-lamellar vesicles that can transform into bigger vesicles with the progression of time. At higher concentrations (above the critical gelator concentration) the individual bilayer vesicles undergo fusion and form an extended superstructured gel. The thus-formed kinetically stable gel slowly transforms, through gliding⁶¹ of the dyad, to thermodynamically stable crystal (Table S1†) over a period of 48 hours (Fig. 4). The metastability (Table S2†) of the (*R*)-NP(OH)₂-containing vesicular gel encouraged us to investigate

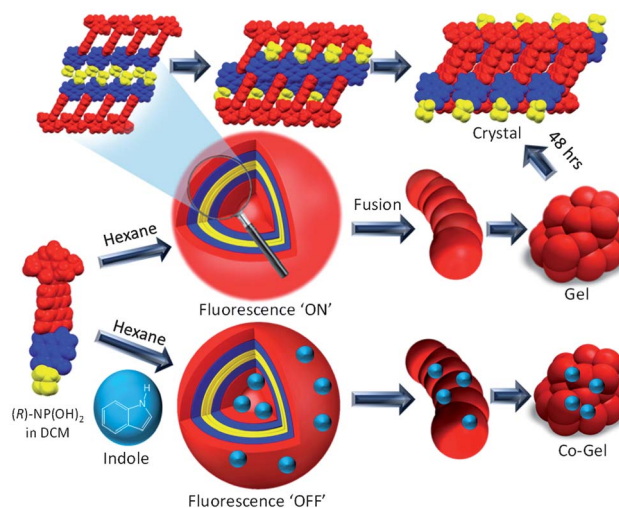


Fig. 4 Mechanism for molecule–bilayer–vesicle–gel–crystal transition. Schematic representation of self-assembly of (*R*)-NP(OH)₂ in a DCM–hexane (1 : 2) mixture in the absence and presence of indole.

the photoinduced processes in the presence of indole (electron donor). The $(R)\text{-NP(OH)}_2$ gel retained its stability even at a 100 : 1 indole : $(R)\text{-NP(OH)}_2$ ratio. The SEM image of 0.1 mM $(R)\text{-NP(OH)}_2$ in the presence of 1 mM indole exhibited spheroidal particles with an average diameter of 160 nm (Fig. 3l). The observed surface roughness in the spheroidal particles could arise from the adsorption of indole molecules on the $(R)\text{-NP(OH)}_2$ vesicle surface. The TEM image of 0.25 mM $(R)\text{-NP(OH)}_2$ in the presence of 2.5 mM indole exhibits spheroidal particles with an average diameter of 400 nm (Fig. 3m). An additional contrast on the vesicular surface, apart from the rim of the spheroidal particles of the $(R)\text{-NP(OH)}_2$ xerogel, confirms the integrity of the vesicles with indole molecules adsorbed on the surface. The optical microscopy image (Fig. 3n) of $(R)\text{-NP(OH)}_2$ vesicles containing indole showed a significant fluorescence quenching indicating the possibility of a photoinduced electron transfer process from the indole to singlet excited states of the chromophoric units.

With increase in indole concentration, the $(R)\text{-NP(OH)}_2$ gel shows up to a 4-fold decrease in the fluorescence quantum yield and a significant decrease in the fluorescence lifetime ($\tau = 0.6$ ns), upon excitation both at 345 nm and 475 nm (Fig. S16[†]). Stern–Volmer analysis⁶² of the steady-state and time-resolved fluorescence data (see ESI[†]) of the $(R)\text{-NP(OH)}_2$ gel with an increase in concentration of indole offered a similar bimolecular quenching rate constant $k_q = 7.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. S17a–d[†]) indicating dynamic quenching of the singlet excited state of perylenimide ($^1\text{PI}^*$). The observed bimolecular quenching rate constant in the case of the $(R)\text{-NP(OH)}_2$: indole co-gel is lower than the upper bound of the diffusional bimolecular quenching constant, $k_q = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ confirming the dynamic nature of the photoinduced electron transfer.⁶³ We observed a similar bimolecular quenching rate constant for the photoinduced electron transfer from indole to the singlet excited state of perylenimide in $(R)\text{-NP(OH)}_2$ solution ($k_q = 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Fig. S18[†]) when compared to the co-gel, consistent with the reported D–A pair.^{64,65} UV-Vis absorption spectra of the dyad $(R)\text{-NP(OH)}_2$ in DCM exhibited a negligible change before and after the addition of indole (1000 equivalents) ruling out the possibility of ground state complexation between the indole and the constituents of the dyad (Fig. S18a[†]). Rehm–Weller analysis⁶⁶ shows a favourable change in free energy for photoinduced electron transfer from the singlet excited state of NI to PI (–0.17 eV) in the dyad NP(OH) as described earlier.⁵⁰ Photoinduced electron transfer from the indole to the singlet excited state of NI (–1.19 eV) and PI (–0.48 eV) units (see ESI[†]) is thermodynamically feasible.

To characterize the transient intermediates generated upon photoexcitation of the $(R)\text{-NP(OH)}_2$: indole solution and co-gel, we have carried out femtosecond transient absorption measurements and analysed the three dimensional ΔA versus time and wavelength spectral data using singular value decomposition (SVD). Femtosecond transient absorption (FTA) spectra of a 0.75 mM $(R)\text{-NP(OH)}_2$ solution exhibited a bleach centered at 570 nm and a mono-exponential decay corresponding to the singlet excited state of perylenimide ($^1\text{PI}^*$) at 615 nm having a lifetime of 3.1 ns, upon excitation at 390 nm

(Fig. S19a and d[†]). A marginal decrease in the fluorescence quantum yield of $(R)\text{-NP(OH)}_2$ ($\Phi_f = 0.75 \pm 0.04$) corresponding to a PI unit when compared to the model perylenimide PI derivative ($\Phi_f = 0.81 \pm 0.03$) indicates the possibility of photoinduced electron transfer from the singlet excited state of NI to PI ($\Delta G_{\text{charge separation}} = -0.17$ eV) having an estimated rate of $k_{\text{charge separation}} = 2.29 \times 10^{12} \text{ s}^{-1}$.⁵⁰ Upon photoexcitation, charge transfer intermediates in the dyad $(R)\text{-NP(OH)}_2$ solution were not observed, suggesting the fact that rate of charge recombination (<110 fs) is much faster than the rate of charge separation, consistent with similar reported dyads.⁴⁷ In the presence of a lower concentration of indole, a dyad $(R)\text{-NP(OH)}_2$: indole (1 : 10) solution exhibited a mono-exponential decay at 617 nm corresponding to $^1\text{PI}^*$ having a lifetime of 2.9 ns, similar to the lifetime of $^1\text{PI}^*$ in the dyad $(R)\text{-NP(OH)}_2$ solution (Fig. S19b and e[†]).⁶⁷ The lack of formation of charge transfer intermediates in the dyad $(R)\text{-NP(OH)}_2$: indole (1 : 10) solution is consistent with insignificant fluorescence quenching corresponding to the dyad $(R)\text{-NP(OH)}_2$ under similar conditions, indicating the absence of photoinduced electron transfer from indole to $^1\text{PI}^*/^1\text{NI}^*$. At higher concentrations of indole, the dyad $(R)\text{-NP(OH)}_2$: indole (1 : 500 and 1 : 1000) solution showed a bleach around 570 nm and two absorption bands centered around 598 nm and 619 nm, upon photoexcitation (Fig. 5b, S19c and f[†]). SVD analysis followed by global fitting offered a lifetime of 6–6.5 ps at 598 nm corresponding to the radical anion of perylenimide ($\text{PI}^{\cdot-}$)^{48,68} and 0.5–0.64 ns at 619 nm corresponding to the singlet excited state of perylenimide ($^1\text{PI}^*$, inset of Fig. 5b and Table S3[†]). The formation of the charge transfer intermediate $\text{PI}^{\cdot-}$ in the dyad $(R)\text{-NP(OH)}_2$ at higher concentrations of indole (1 : 500 and 1 : 1000) solution signifies the occurrence of diffusion-controlled photoinduced charge separation⁶⁹ that is consistent with the quenching of fluorescence of the dyad $(R)\text{-NP(OH)}_2$ (Fig. S18b and d[†]). Greater dependence on the distribution of charged intermediates with increase in concentration of the electron donor indole indicates that the rate of charge separation dominates over rate of charge recombination ($k_{\text{cs}} > k_{\text{cr}}$).⁷⁰

Nanosecond transient absorption spectroscopic measurements of dyad $(R)\text{-NP(OH)}_2$: indole (1 : 500 and 1 : 1000) in DCM failed to detect the presence of charged intermediates, upon excitation at 355 nm and 532 nm. Lack of transient intermediates in the nanosecond transient absorption measurements of the dyad $(R)\text{-NP(OH)}_2$: indole could be attributed to ultrafast charge recombination occurring faster than the time-resolution of the instrument (≥ 10 ns). The observed short lifetime (*ca.* 6 ps) of the radical anion of perylenimide ($\text{PI}^{\cdot-}$) from FTA measurements is consistent with the short-lived coumarin–amine based solvent separated radical ion pair (SSRIP) formed through diffusion controlled intermolecular photoinduced electron transfer as reported earlier.⁷¹ Self-assembled vesicular architecture in the dyad $(R)\text{-NP(OH)}_2$ gel exhibits a similar monoexponential decay of $^1\text{PI}^*$ ($\tau = 2.9$ ns; Fig. 5a and inset of 5a for singular vector) at 620 nm upon photoexcitation. In contrast to an extension in the photoinduced charge separation lifetimes of an assembled guanine–perylene diimide G-quadruplex structure⁴⁷ and a melamine–peryleneimide based foldamer⁴⁸ reported

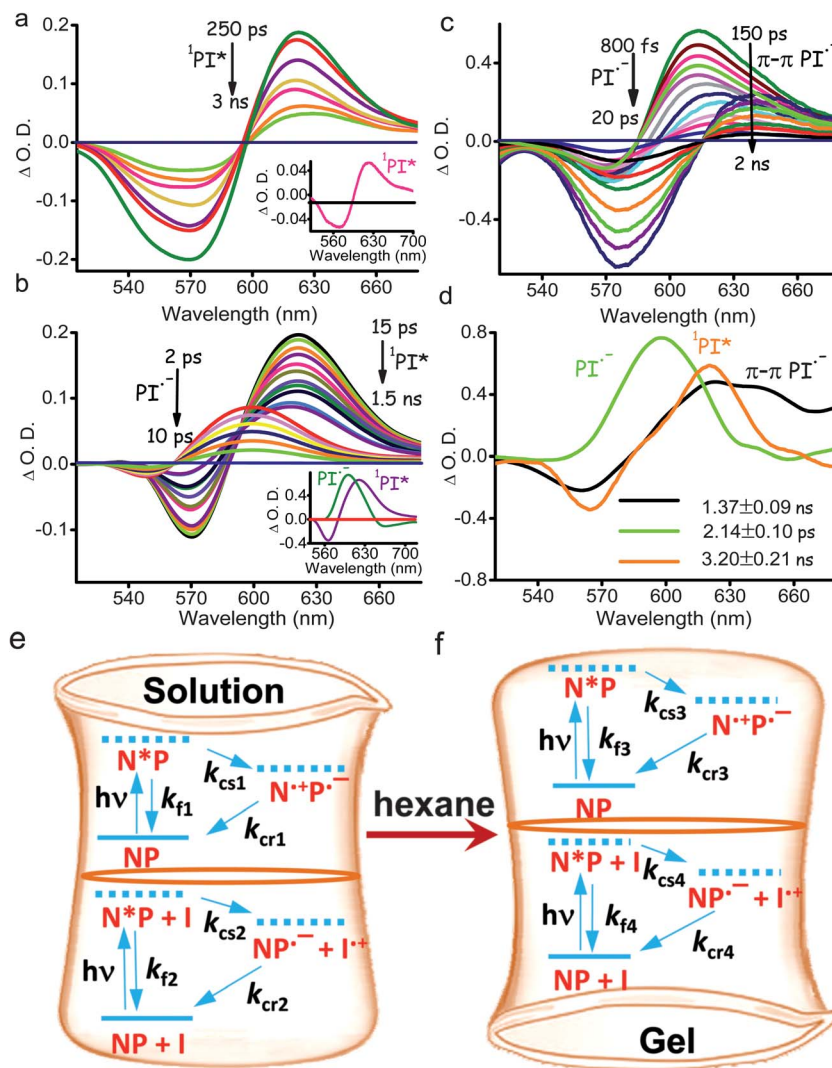


Fig. 5 Ultrafast kinetics and Jablonski diagram showing the reduced rate of charge recombination in the (R)-NP(OH)₂: indole co-gel. Femtosecond transient absorption (Δ OD) spectra of (a) (R)-NP(OH)₂ gel, inset shows the principal component of the spectra obtained from SVD; (b) (R)-NP(OH)₂ solution in presence of 1000 equivalents of indole in DCM, inset of (b) shows the principal components of the spectra obtained from SVD; (c) (R)-NP(OH)₂: indole co-gel excited at 390 nm; (d) principal components of the spectra shown in (c) from SVD; Jablonski diagram of the (R)-NP(OH)₂ in the absence and presence of indole (I) in (e) solution and (f) gel.

by Wasielewski and co-workers, the absence of charge transfer intermediates in the dyad (R)-NP(OH)₂ gel could be attributed to ultrafast charge recombination of $\text{PI}^{\cdot-}$ and $\text{NI}^{\cdot+}$ in <110 fs.

SVD analysis followed by global fitting of the FTA spectra of the dyad (R)-NP(OH)₂: indole (1 : 10) co-gel (Fig. 5c) yielded three principal components of the spectra, as illustrated in Fig. 5d. The three principal components obtained from SVD could be assigned as the following: (i) the radical anion of perylenimide ($\text{PI}^{\cdot-}$)^{48,68} and/or the radical cation of indole ($\text{I}^{\cdot+}$) centered at 597 nm with a lifetime of 2.1 ps;^{72,73} (ii) the singlet excited state of perylenimide ($^1\text{PI}^*$)^{67,74} featured at 620 nm with a lifetime of 3.0 ns; and (iii) radical anion of π - π stacked perylenimide (π - π $\text{PI}^{\cdot-}$) at 640 nm with a lifetime of 1.4 ns.⁴⁸ We observed a time-dependent shift in the peak corresponding to the decay of $\text{PI}^{\cdot-}$ indicating the evolution of a radical anion of larger π - π stacks of perylenimide (Fig. 5c).^{48,75} An increase in

the survival time of $\text{PI}^{\cdot-}$ in the dyad (R)-NP(OH)₂: indole co-gel indicates sequential electron transfer from the singlet excited state of naphthalimide ($^1\text{NI}^*$) to PI followed by an electron transfer from indole to $\text{NI}^{\cdot+}$ upon excitation of the NI unit. Alternatively, $^1\text{PI}^*$ formed *via* energy transfer from $^1\text{NI}^*$ can abstract an electron from indole leading to the formation of $\text{PI}^{\cdot-}$ and a radical cation of indole. The lifetime of $\text{PI}^{\cdot-}$ is found to be comparable in the dyad (R)-NP(OH)₂: indole (1 : 10) co-gel and in the dyad (R)-NP(OH)₂: indole (1 : 1000) solution, indicating photoinduced charge separation followed by fast charge recombination (*ca.* 2–6 ps). Meanwhile, the longer survival time of the charge transfer intermediate arising from π - π $\text{PI}^{\cdot-}$ (*ca.* 1.4 ns) in the dyad (R)-NP(OH)₂: indole (1 : 10) co-gel, which is absent in the dyad (R)-NP(OH)₂: indole (1 : 1000) solution, could be attributed to the favourable supramolecular arrangement of the donor-acceptor systems for efficient charge

separation followed by slow charge recombination. A remarkable increase in the survival time of π - π $\text{PI}^{\cdot-}$ in $(R)\text{-NP(OH)}_2$ gel (Fig. 5c and f) vs. solution (Fig. 5e) in the presence of indole could be attributed to the decrease in the rate of diffusion of transient intermediates in a highly viscous medium (gel) resulting in slower rate of charge recombination (k_{cr4}) compared to the solution (k_{cr2}), as reported in the self-assembled systems.^{39,76}

The Jablonski diagram in Fig. 5e and f demonstrates competitive deactivation pathways of the singlet excited state *via* fluorescence and electron transfer states of the dyad $(R)\text{-NP(OH)}_2$ upon photoexcitation under different conditions. Analysis of time-resolved fluorescence and femtosecond transient spectroscopic data revealed that $k_{\text{cs1,3}} \lll k_{\text{cr1,3}}$, respectively, and hence intrinsic fluorescence decay predominates over charge separation in the $(R)\text{-NP(OH)}_2$ solution/gel. At a lower concentration of indole, $(R)\text{-NP(OH)}_2$ in DCM exhibited a negligible decrease in the fluorescence quantum yield indicating the lack of forward electron transfer from indole to $^1\text{PI}^*/^1\text{NI}^*$ through bimolecular processes ($k_{\text{q}}[\text{M}] \ll k_{\text{f}}$; Table S3[†]). At higher concentrations of indole, the rate of bimolecular quenching is comparable to the rate of fluorescence ($k_{\text{q}}[\text{M}] \approx k_{\text{f}}$; Table S3[†]) resulting in efficient photoinduced electron transfer from indole to $^1\text{PI}^*/^1\text{NI}^*$. Meanwhile, in the case of the $(R)\text{-NP(OH)}_2$: indole co-gel (1:10), the rate of bimolecular quenching could compete with the intrinsic decay of the singlet excited state thereby resulting in efficient photoinduced charge separation ($k_{\text{q}}[\text{M}] \approx k_{\text{f}}$; Table S3[†]) followed by slow charge recombination ($k_{\text{cr}} \ll k_{\text{cs}}$; Table S3[†]). A significant decrease in the rate of charge recombination could be a consequence of the extended charge delocalisation through a supramolecular π - π stacked arrangement of perylenimide units in the $(R)\text{-NP(OH)}_2$: indole co-gel.

Conclusions

In summary, the amphiphilic nature offered by the chiral side-chain (lyophobic) and orthogonal naphthalimide–peryleneimide unit (lyophilic) in $(R/S)\text{-NP(OH)}_2$ in DCM forces the molecules to form a bilayer vesicle with an increase in the volume fraction of hexane. We observed growth of the vesicles followed by fusion to form a superstructured gel with an increase in concentration of the dyad $(R/S)\text{-NP(OH)}_2$ and progress of time. The metastable nature of the gel forces the dyad $(R/S)\text{-NP(OH)}_2$ to undergo gliding, resulting in a thermodynamically stable crystal. Highly efficient energy transfer from the naphthalimide to the perylenimide unit upon excitation at 345 nm and direct excitation of the perylenimide unit ($\lambda_{\text{ex}} = 475$ nm) in the vesicular gel makes this dyad $(R/S)\text{-NP(OH)}_2$ an excellent light-harvesting assembly. Upon photoexcitation, a remarkable decrease is observed in the rate of charge recombination of the transient intermediates in $(R/S)\text{-NP(OH)}_2$ gel in the presence of an electron-donor when compared to a $(R/S)\text{-NP(OH)}_2$: indole solution. The enhanced survival time of the radical intermediates in the $(R/S)\text{-NP(OH)}_2$: indole co-gel is an effect of a favourable supramolecular arrangement that stabilises the radical anion of perylenimide in a π - π stacked self-assembled structure of

$(R/S)\text{-NP(OH)}_2$, a feature that is inaccessible in non-assembled D–A systems based on photoinduced charge separation. Sequential photoinduced energy/electron transfer processes followed by delayed charge-recombination in solution processable self-assembled donor–acceptor arrays are essential for the fabrication of photovoltaic devices and artificial photosynthesis.

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