Supporting Information

Assemblies of Perylene Diimide Derivatives with Melamine into Luminescent Hydrogels

Pradip Kumar Sukul, Deepak Asthana, Pritam Mukhopadhyay, Domenico Summa, Luca Muccioli, Claudio Zannoni, David Beljonne, Alan E. Rowan and Sudip Malik

Table of Contents

1) Materials and Methods	S3
2) Synthesis and characterization of PI and PBI	S4-S6
3) Instruments and Experimental Techniques	S7-S8
4) Additional photos of gel	S9
5) Additional FE-SEM images	S10
6) UV-Vis absorption results of PI/MM system	S11-S13
7) Determination of stoichiometry	S14
8) CLSM images	S15
9) Fluorescence life time data	S16
10) NMR studies	S17
11) FTIR results	S18
12) XRD results	S19
13) UV-Vis absorption results of PBI/MM system	
14) Fluorescence results of PBI and PBI/MM systems	
15) Molecular dynamics and simulations details	S24-S30
16) References	

1) Materials and methods

Reagents were purchased from sigma-aldrich and used as received. 1,7-dibromo-perylene-3,4:9,10-tetracarboxylic Dianhydride, PI and PBI had been synthesized using literature procedure.^{S1,S2} For all aqueous mixtures and for spectroscopic studies, water of spectroscopic or HPLC grade was used.

¹H-NMR spectra were recorded at room temperature on 300 and 500 MHz spectrometers (Bruker). ¹H NMR chemical shifts (δ) were reported in parts per million (ppm) ¹H NMR shifts were referenced to the residual hydrogen peak of D₂O (4.70 ppm). Splitting patterns were denoted *s* (singlet), *br*. (broad). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was carried out with Bruker Daltonics FLEX-PC using diathranol as a matrix. FT-IR spectra were recorded using KBr pellets of samples in an FTIR-8400S instrument (Shimadzu).

2) Synthesis and characterization of PI and PBI



Scheme S1. Synthesis of **PI and PBI**. Reagents and conditions: (a) 5-aminoisophthalic acid, imidazole, 6 h, 127^{0} C, 85%; (b) H₂SO₄, I₂, Br₂, 75%; (c) 5-aminoisophthalic acid, imidazole, 6 h, 127^{0} C, 74%.

Synthesis of N, N'-Di-(phenyl-3, 5-dicarboxylic acid)-perylene-3,4:9,10-tetracarboxylic acid diimide(PI):

1gm (2.55 mmol) of perylene-3,4:9,10-tetracarboxylic dianhydride, 1.154 gm (6.37 mmol) 5aminoisophthalic acid and 8 gm of imidazole were heated at 127^{0} C for 6 hrs under nitrogen atmosphere. Then 100 mL of ethanol was poured into the hot mixture, refluxed for 6 hrs and kept for overnight to precipitate out. The precipitate was filtered and washed with ethanol. The product was dried at 70^{0} C under vacuum oven to get 1.56 gm deep red powder (Yield: 85%). ¹H NMR of PI(300 MHz , D₂O,25^oC) ∂ : 8.54 (s,2H) , 8.13 (s,4H) , 7.21 (m , 8H) IR (KBr) $v_{max} = 744$, 808, 852, 1114, 1252, 1355, 1575, 1662, 1699, 2924, 3147 cm⁻¹. MS (MALDI-TOF): m/z calc. for C₄₀H₁₈N₂O₁₂: 718.58, found: 741.12 [M+Na⁺].

UV/Vis (H₂O): λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) 533 (27436), 496 (19523) , 465 (9801).

Fluorescence (H₂O): λ_{max}/nm : 550, 594, Fluorescence quantum yield (Φ_{f}) = 0.19.

Synthesis of 1,7-Dibromoperylene-3,4:9,10-bis(dicarboxylic anhydride) :

3,4:9,10-perylenetetracarboxylic dianhydride (2 gm, 5.10 mmol) was added to 30 mL concentrated sulfuric acid and stirred at 55° C for 24 hrs. Iodine (0.048 gm, 0.189 mmol) was added to the reaction mixture and stirring for an additional 5 hrs at 55° C. Bromine (0.6 mL, 11.71 mmol) was added drop wise to the reaction flask over the course of 1 h and the reaction mixture stirred for 24 h at 85° C. Excess bromine was then displaced with a N₂ stream. Water (20 mL) was next added drop wise to the cooled mixture and the resulting precipitate collected by filtration. The crude product was next washed with 86 % H₂SO₄ followed by water to afford crude product of 1.05 gm (75%). The crude product was then dried under reduced pressure at 120 °C and used for the next step without further purification.

FT-IR (KBr): 1766.67, 1593.09, 1506.30, 1402.15

MS (MALDI-TOF): 550.12 (calcd. 550.11, M)

Fluorescence quantum yield (Φ_f) =0.23.

Synthesis of N, N'-Di-(phenyl-3, 5-dicarboxylic acid)-1, 7-dibromoperylene-3, 4:9, 10-tetracarboxylic acid diimide (PBI):

Similar procedure as like preparation of PI was followed for the synthesis of PBI (yield: 1.48g, 74%.)

¹H NMR (300 MHz, D₂O, 25 °C) ∂ : 8.35 (s , 2H) , 7.99 (s , 4H) , 7.06 (m , 6H).

IR (KBr) $v_{max} = 745, 809, 852, 1179, 1255, 1357, 1575, 1661, 1699, 2833, 3142 \text{ cm}^{-1}$.

MS (MALDI-TOF): m/z calc. for C₄₀H₁₆Br₂N₂O₁₂: 876.37, found: 877.44 [M+H⁺]

UV/Vis (H₂O): $\lambda_{max}/nm (\epsilon/M^{-1}cm^{-1})$ 533 (42883), 496 (30081), 465(13455).

Fluorescence (H₂O): λ_{max}/nm : 550, 592, Fluorescence quantum yield (Φ_{f}) = 0.36.

3) Instruments and Experimental Techniques

3.1. Optical Measurements

The UV-Vis spectra of all samples were studied with Hewlett-Packard UV-Vis spectrophotometer (model 8453). Temperature dependent studies were carried out in a 0.1cm quartz cuvette with a thermistor directly attached to the wall of the cuvette holder at a heating rate of 2 °C /min. Fluorescence studies of solution and hydrogel samples, prepared in a sealed cuvette, were carried out with Horiba Jobin Yvon Fluoromax 3 instrument at excited wavelength 475 nm. The quantum yields of fluorophore were determined by applying the Parker-Rees method and using *Rhodamine 6G* solution in water (λ_{abs} = 536 nm, λ_{em} = 550 nm, φ = 0.95) as reference.^{S3, S4}

3.2. Field Emission-Scanning Electron Microscope (FE-SEM)

To understand the morphology of the gel, small portions of the hydrogels were placed on glass cover slip and were dried in air at room temperature, finally in vacuum at 25° C. It was coated with platinum for 60 sec prior to observation through a FESEM instrument (JEOL, JSM 6700F) operating at 5 KV.

3.3. Atomic Force Microscopy (AFM)

AFM studies were conducted using atomic force microscopy (Veeco, model AP0100) in noncontact mode at a tip resonance frequency of 300 kHz. Samples for the imaging were prepared by drop casting the **PI-MM=1:2** solution on freshly cleaved mica surface at the required concentrations at ambient conditions.

3.4. Confocal Laser Scanning Microscope (CLSM)

Confocal laser scanning microscope (CLSM) images were taken with Leica laser scanning confocal microscope (Leica confocal system TCS-SP2 instrument) equipped with an ArKr laser under 100X magnification at an excitation wavelength 488 nm.

3.5. NMR Titration:

¹H NMR titration were performed at room temperature on 500 MHz spectrometers (Bruker) using a solution of PI in D₂O at a concentration of 1.2×10^{-3} M. Subsequently MM solution in D₂O at a concentration of 6×10^{-3} M was added from 1:0 to 1:1.8 molar ratios (PI: MM).

3.6. Fluorescence lifetime measurement:

Fluorescence lifetimes were measured by using a time-correlated single photon counting fluorometer (Fluorecule, Horiba Jobin Yvon). The system was excited with a 440 nm NanoLED from Horiba Jobin Yvon having λ_{max} at 452 nm with a pulse duration of <200 ps. All solutions prepared at room temperature (25°C) were deoxygenated by purging with argon gas for 30 min prior to measurement.

4) Photos of gel (Bottle inversion)



Fig. S1: (a) Photo of melamine (MM) solution, PI/MM=1:2 hydrogel, and PI solution in water (b) Photo PBI/MM=1:2 hydrogel.

5) FE-SEM images



Fig. S2: FE-SEM images, (a) for only PI ($[PI]=10^{-2}M$), (b) for PI:MM=1:2 gel ($[PI]=10^{-2}M$), (c) for PI:MM=1:2 ($[PI]=2.5\times10^{-4}M$), and (d) for PBI:MM=1:2 gel ($[PBI]=10^{-2}M$).





Fig. S3: Concentration dependent UV-Vis spectra of **PI/MM=1:2** at 20⁰C at different concentration.



Fig. S4: (a) Time dependent UV-Vis spectra of **PI/MM=1:2** at a concentration of [PI] $= 2.5 \times 10^{-4}$ M, and (b) Trace plot for **PI/MM=1:2** at three wavelengths.



Fig. S5: Temperature dependent UV-Vis spectra of (a) only **PI** and (b) **PI/MM=1:2** at a $[PI] = 2.5 \times 10^{-4}$ M (black line at 20^oC and yellow line at 80^oC). Isosbestic points are at 471 and 558 nm.

7) Determination of stoichiometry



Fig. S6: Fluorescence spectra of PI with different molar equivalent of MM at room temperature, $[PI] = 10^{-3}M$, $\lambda_{ex}=475$ nm, [pathlength = 10 mm]. Inset: plot of emission intensity at 612 nm vs [MM]/[PI].

8) CLSM Images



Fig. S7: CLSM images of PI/MM = 1:2 hydrogel (a) and the corresponding optical microscopic image (b). The same for PBI/MM = 1:2 hydrogel (c) and the corresponding optical microscopic images (d).

9) Fluorescence lifetime results:

Table S1: Fluorescence decay times (τ , ns) and their relative amplitude (α) obtained from fluorescence decay profile. The average life time has calculated using the equation.^{S3.S4}

$$\left\langle \tau \right\rangle_{adv} = \frac{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3}{100}$$

	λ_{em}	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$\alpha_1(\%)$	$\alpha_2(\%)$	α ₃ (%)	<τ>
	(nm)							(ns)
PI solution	732	1.37	3.37	0.35	49	23	28	1.54
PI-MM solution	679	1.42	3.96	0.38	46	32	22	2.0
PI/MM gel	679	0.51	4.27	-	-2	102	-	4.27

10) NMR studies



Fig. S8: (a) ¹H NMR titration of MM from 0 to 1.8 equiv into PI (1.2 mM) in D₂O at 298 K. (b) plot of chemical shift (δ) of aromatic hydrogen atoms vs the equivalent of MM added to PI solution in D₂O at 298 K [H^a and H^b indicate the proton on perylene core and benzene moiety of PI].

11) FT-IR Studies



Fig. S9: (top) FT-IR spectra diluted with KBr for (a) pure PI, (b) pure MM, (c) PI/MM=1:1 dried gel, and (d) PI/MM=1:2 dried gel, and (bottom) FT-IR spectra for (a) pure PBI, (b) PBI:MM=1:2 dried gel and (c) pure MM.

Electronic Supplementary Material (ESI) for Chemical Communications This journal is The Royal Society of Chemistry 2011

12) XRD results



Fig. S10: X-ray diffraction traces of (a) MM, PI and PI/MM dried gels. (b) MM, PBI, PBI/MM dried gel. In X-ray diffraction (XRD) powder patterns, interestingly, only the dried gel of PI/MM exhibits distinctive peaks at 2θ =24.5, corresponding to a d-spacing of 3.6Å, that is, a typical π - π stacking distance. This result supports the involvement of well-defined intermolecular π - π interactions between PI in nanofibers. Whereas, PBI/MM system this diffraction peak is broad, indicating the inhibition of π - π interactions due to presence of bromine atoms at bay position of perylene.



13) UV-Vis absorption results of PBI/MM system

Fig. S11: Concentration dependent UV-Vis spectra of PBI/MM=1:2 at 20° C at different concentration.



Fig. S12: (a) Time dependent UV-Vis spectra of PBI/MM=1:2 at a $[PBI] = 2.5 \times 10^{-4}$ M, and (b) times traces at three wavelengths.



Fig. S13: Temperature dependent UV-Vis spectra of (a) only PBI and (b) PBI/MM=1:2 at a [PBI] = 2.5×10^{-4} M (black line at 20° C and yellow line at 80° C). Isosbestic points are at 465 and 558 nm.



14) Concentration dependent fluorescence results of PBI and PBI/MM

Fig. S14: Concentration-dependent fluorescence spectra of (a) **PBI** solution and (b) **PBI/MM=1:2** solution in water at 25^oC and $\lambda_{ex} = 475$ nm. (**[PBI]** in both figures = 1.25×10^{-6} M (purple), 2.5×10^{-6} , 3.75×10^{-6} , $5x10^{-6}$, 1.25×10^{-5} , 2.5×10^{-5} , 3.75×10^{-5} , $5x10^{-5}$, 1.25×10^{-4} , 2.5×10^{-4} , 3.75×10^{-4} , $5x10^{-4}$ (black). Arrows indicate spectral change upon increasing concentration. [Inset: PBI only and fluorescent PBI/MM hydrogels under UV irradiation at 365 nm].

15) Molecular Dynamics Simulations Computational Details

All the Molecular Dynamics simulations were run with the NAMD code,^{S5} with 3D periodic boundary conditions using the GAFF^{S6} force field for PI and melamine (MM) and TIP3P water model as a solvent.^{S7} Atomic charges for PI and MM, were calculated at PBE0//cc-pVTZ density functional theory level. The torsional potential for the rotation about the dicarboxyl-phenyl-diimide and the NH₂-triazine bonds (Fig. S15) were calculated at the same level of theory and implemented in the force field as described by Pizzirusso *et al.*^{S8} The adopted force field is known to adequately describe (dynamic) H-bonding in solution without need of resorting to explicit H-bond terms.^{S9}





Fig. S15: Torsional potential for melamine C-NH2 torsion (blue squares) and PI N-dicarboxylphenyl (green circles) calculated at PBE0/aug-cc-pVTZ slevel.

Fig. S16: Four selected oppositely charged pairs in a stack

The interaction cut off for VdW forces was set to 10 Å, while for long-range electrostatic interactions we used the particle mesh Ewald method.^{S10} The standard time step of 1 fs was used. Simulations were run in ambient conditions, i.e. at constant pressure p=1 atm and temperature T=300 K, using Berendsen's barostat and thermostat and a cubic cell.^{S11}

In a preliminary simulation we tested for 10 ns the self aggregation in solution of 60 PI and 120 MM dissolved in 32500 water molecules, obtaining short stacks of PI glued together by MM.

A 13 PI self-assembled stack was then replicated four times in space (52 molecules) and equilibrated in water (7500 molecules), in presence and in absence of MM (104 molecules) for 20 ns. The comparison between the two stacks indicated multiple roles for MM, which: i) acts as linker between PI molecules through the specific interactions with the carboxyl groups, ii) may intercalate in the stack, iii) can increase positional disorder by shifting apart PI molecules, iv) confers rigidity to the stack limiting the twisting motion.^{S12}

The geometrical changes that may occur in the stacks upon formation of charge-transfer excimer

were probed in a third series of simulations, using the configurations described above as a starting point and following the dynamics for 20 further ns. In this case, four selected PI dimers in the column, separated in space, were endowed of a positive and a negative charge (Fig. S16), opportunely rescaling the atomic charges of the aromatic core. To improve the statistics of the results, the scheme was repeated five times, each time choosing different dimers, with and without MM.

Time-Dependent density functional theory results for PI dimers

A "typical" dimer was extracted from a 52-molecules PI stack (equilibrated at room temperature with 7500 water molecules), and optimized at B97D/6-31G level.^{S13} At the final geometry (Fig. S17), PI aromatic cores are parallel, while the lateral dicarboxyl-phenyl groups are on one side parallel, and on the other tilted in opposite directions to form an hydrogen bond between two carboxyl groups. Both situations are very frequent during the molecular dynamics simulation of the stack. The intermolecular distance is about 3.4 Å, the twist angle 22-27 degrees (depending on the atoms chosen to measure it), and the lateral shift around 1.5 Å.

To save computational resources, the side groups were then replaced by hydrogens and the geometry re-optimized by fixing the distances between the core hydrogens and the central carbons of the two molecules, in order to maintain the twist angle and the relative in-plane translation inherited by the presence of the dicarboxyl-phenyl groups.

We then carried out a series of TDDFT excited-state single-point calculations based on this ground state geometry and systematically varying from 3 to 6 Å the distance between the two perylene diimides constituting the dimer, with the purpose of identifying the role of this geometrical parameter on the stabilization of a charge-transfer state which may suppress the fluorescence emission of the PI stack in absence of MM. All calculations were performed with the Gaussian09 package.

We employed three different hybrid functionals alongside the cc-pVDZ basis set: the widely used B3LYP,^{S14} BHandHLYP, known to be more effective than B3LYP in the description of CT states,^{S15} and the more modern, long-range corrected wB97XD.^{S16} The different quality of the description of intermolecular interaction is well shown by the plot of the intermolecular energy in Figure S18: while for B3LYP the interaction between two PI is purely repulsive, and only a very feeble minimum is predicted by BHandHLYP, more realistically wB97XD suggest a substantial interaction of ~30 kcal/mol at ~3.4 Å.



Fig. S17: PI dimer geometry optimized at B97D/6-31G level.



Fig. S18: PI dimer ground state energy as function of the intermolecular distance calculated at TDDFT level and aug-ccVDZ basis set with three different functionals.

The failure of B3LYP is even more dramatic from the excited state properties shown in Fig. S19: a partial or total CT first excited state is predicted at all distances, and its CT character, measured as the sum of either Mulliken or ESP charges, counterintuitively increases with distance. As a direct consequence, the oscillator strength is almost zero, and the radiative decay rate (evaluated with the Strickler-Berg equation in a medium with refractive index n=1) becomes zero at increasing distances, contrary to the experimental observation of the quenching of fluorescence upon aggregation. BHandHLYP and wB97XD results are more physically meaningful (Fig. S20 and Fig. S21) are and consistent with the INDO/SCI data reported in the main text, and predict a partial charge transfer (higher for wB97XD) only at distances below 3.6 Å. Finally in Fig. S22 the impact of the in-plane rotation of the dimers (twist) was evaluated with the wB97XD functional at short interplanar distances: the CT nature of the excited state is not strongly affected by this rotation, except in the region around 90 degrees, which however is not likely to be populated in the stack (the equilibrium twist angle being around 30 degrees).









16) References

S1. B. A. Jones, M. J. Ahrens, M. H. Yoon, A. Facchetti, T. J. Marks, M. R. Wasielewski, *Angew. Chem. Int. Ed.*, 2004, **43**, 6363.

S2. R. Sun, C. Xue, M. Owak, R. M. Peetz, S. Jin, Tetrahedron Lett., 2007, 48, 6696.

S3. J. N. Dames, G. A. Crosby, J. Phys. Chem., 1971, 75, 991.

S4. C. A. Parker, W. T. Rees, Analyst, 1962, 87, 83.

S5. J. C. Phillips, R. Braun, W. Wang, J. Gumbart, E. Tajkhorshid, E. Villa, C. Chipot, R. D. Skeel, L. Kale, K. J. Schulten, *Comput. Chem.*, 2005, **26**, 1781.

S6. L. Yang, C. Tan, M.-J. Hsieh, J. Wang, Y. Duan, P. Cieplak, J. Caldwell, P. A. Kollman, R. Luo, *J. Phys. Chem. B*, 2006, **110**, 13166.

S7. W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, M. L. Klein, J. Chem. Phys., 1983, 79, 926.

S8. A. Pizzirusso, M. Savini, L. Muccioli, C. Zannoni, J. Mater. Chem., 2001, 21, 125.

S9. A. D. Mackerell, J. Comput. Chem., 2004, 25, 1584.

S10. U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, L. G. Pedersen, J. Chem. Phys. 1995, 103, 8577.

S11. H. J. C. Berendsen, J. P. M. Postma, W. F. Van Gunsteren, A. Di Nola, J. R. Haak, *J. Chem. Phys.*, 1985, **81**, 3684.

S12. D. Summa, L. Muccioli, C. Zannoni, D. Beljonne, P. K. Sukul, S. Malik, A. E. Rowan, Manuscript in preparation, 2011.

S13. S. J. Grimme, Comp. Chem., 2006, 27, 1787.

S14. D. J. Becke, Chem. Phys., 1993, 98, 1372.

S15. R. J. Magyar, S. J. Tretiak, Chem. Theory Comput., 2007, 3, 976.

S16. J.-D. Chai, M. Head-Gordon, Phys. Chem. Chem. Phys., 2008, 10, 6615.