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ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 11858–11860

www.rsc.org/chemcomm

COMMUNICATION

Assemblies of perylene diimide derivatives with melamine into luminescent hydrogels†

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Received 12th July 2011, Accepted 2nd September 2011
DOI: 10.1039/c1cc14189a

We report unique and spontaneous formation of hydrogels of perylene derivatives with melamine. The luminescent gel network is formed by H-type aggregation of the perylene core, supramolecularly cross-linked by melamine units. As a result of controlled aggregation in the extended nanofibers, strong exciton fluorescence emission is observed.

The study of molecular gels[1] has recently become an area of great interest in the fields of supramolecular chemistry and material science. Small molecules are held together by non-covalent interactions such as hydrogen bonds, π–π interactions, dipole–dipole interactions, van der Waals forces, solvophobic interactions *etc.* These interactions are much advantageous for the creation of various kinds of smart materials due to their dynamic character. In particular, hydrogels are of great importance due to their potential applications in drug delivery,[2] tissue engineering,[3] and biosensing.[4a]

Perylenediimide dyes are an interesting class of chromophores and fluorophores due to their enhanced stability, good optical properties and pronounced capabilities of self-assembly by means of π–π stacking. These are also the basic materials of numerous organic electronics for light emitting diodes, field effect transistors and photovoltaic cells.[5] Owing to pronounced hydrophobicity of perylene derivatives due to the presence of an aromatic perylene core, their usage in an aqueous environment has been restricted.[6] There have been tremendous efforts directed towards the design and synthesis of perylene based gelators. Shinkai *et al.*[4b] reported light harvesting organogel of cholesterol based perylene derivatives, whereas, Würthner *et al.*[7] developed a super organogelator from perylene derivatives with J-type aggregation. Even, stimuli responsive supramolecular gels of perylene derivatives have been reported by Rybtchinski *et al.*[8] All these gelation studies were carried out in organic medium. To the best of our knowledge, there is no report on gelation of perylene derivatives in water. Utilizing a rational design, herein we report a two-component based spontaneous hydrogelation of perylene derivatives with melamine (MM).[9]

Two derivatives (PI and PBI) have been designed (Fig. 1a), synthesized and unambiguously characterized. These are water soluble due to the presence of four carboxylic acid groups. Typically, hydrogels are prepared by mixing of the solution of PI in water (2×10^{-2} M) with the solution of MM in water (4×10^{-2} M) at equal volume ratio. Spontaneous gel is formed for PI at comparatively low concentration (0.9% w/v) as it is evidenced from the retardation of flow of mixture upon inverting the vials.[10] Spontaneous super-hydrogelation of a two component based system is extremely rare in the literature.[7b,11]

FE-SEM images (Fig. 1b) of dried PI/MM gels reveal that they are composed of long and bundled fibers that form highly dense entangled networks. The average diameter of the fiber is in the range of 20–200 nm. AFM studies of these loose gels

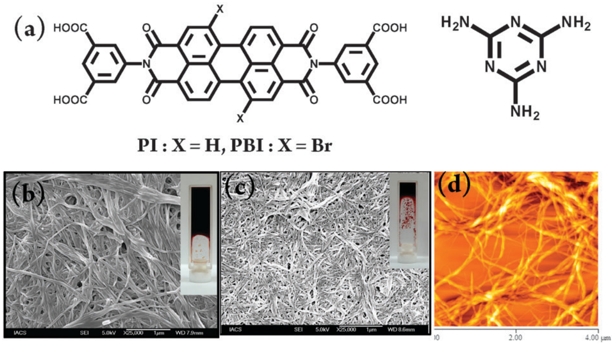

Fig. 1 (a) Molecular structure of PI, PBI and melamine (MM). FE-SEM images of dried gels (b) [PI]/[MM] = 1 : 2 and (c) [PBI]/[MM] = 1 : 2 [PI] or [PBI] = 2×10^{-2} M and [MM] = 4×10^{-2} M [inset: picture of an inverted quartz cuvette of 10 mm pathlength]. (d) AFM topology of loose gel [PI]/[MM] = 1 : 2 directly cast on a freshly cleaved mica surface.

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† Electronic supplementary information (ESI) available: Experimental details for synthesis and characterization of PI and PBI, supplementary figures and molecular dynamics results. See DOI: 10.1039/c1cc14189a

show the presence of individual nanofibers having a diameter of ~12 nm (Fig. 1d). These short fibers are coiled to form bundle of fibers having larger diameters and lengths (5–10 μm) as shown in FE-SEM observations. The formation of gel fiber is presumed to be the result of cross-linking by the MM (H-bonding) between the π-stacked PI units, coated with a water soluble carboxylic acid.

UV-Vis investigations reveal that PI in aqueous medium has a different aggregation behavior in the presence of MM which is optically silent over the region of 400–600 nm. PI having concentration ~2.5×10^{-4} M shows two intense absorption maxima at 502 nm (aggregated band) and 535 nm (monomeric band). After mixing of PI with MM at a molar ratio of 1 : 2, the position of these two maxima remains constant and a new absorption maximum emerges at a lower wavelength, 452 nm (Fig. 2a). The simultaneous formation of a loose gel is confirmed by the naked eye. The generation of a blue-shifted absorption peak at the lower wavelength region indicates a H-type aggregation of the perylene core in the hydrogel. Upon dilution of loose gel of PI/MM (2.5×10^{-4} M to 3.75×10^{-5} M), the inversion of intensities of two bands at 502 nm and 535 nm is observed and concomitantly the 452 nm peak is shifted to 468 nm (Fig. S3, ESI†), indicating monomer absorption. Time dependent plots for PI/MM at [PI] = 2.5×10^{-4} M indicate the gradual increase of intensity of the 452 nm band with decreasing intensities of 502 nm and 535 nm bands (Fig. S4, ESI†). Temperature dependent aggregation of PI/MM [2.5×10^{-4} M] shows the presence of isosbestic points at 471 and 558 nm, revealing a clear transition between spectroscopically different states (Fig. S5, ESI†).

Fluorescence spectra (Fig. 2b) of the gel phase of PI/MM = 1 : 2 ($C_{\mathrm{PI}} = 1 \times 10^{-2}$ M) show the broad emission peak at 677 nm with highly enhanced fluorescence intensity as compared to PI only under identical conditions. It is intriguing to note that the emission is optimum at 1 : 2 and decreases steeply upon adding an additional amount of MM (Fig. S6, ESI†). Upon irradiation at 365 nm, the PI/MM gel emits a bright yellow fluorescence, whilst a solution of PI at the same concentration in the absence of MM generates no visible fluorescence. Concentration dependence of fluorescence sspectra of PI and PI/MM (1 : 2) (Fig. 3a and b) reveals that for the former solution a broad structureless emission band between 600–800 nm arises at high concentration. In contrast, for PI/MM (1 : 2) a defined blue shifted emission is seen with respect to PI solution.[7,12] The luminescent network of gels can be clearly observed under a confocal laser scanning microscope upon excitation at 488 nm (Fig. 3c).[10] Moreover, the emission decay profile observed with nanosecond time-resolved fluorescence shows the increase of life time in the gel state (4.27 ns) with respect to PI (1.54 ns) or PI/MM solution (2.00 ns) in water (Fig. 3d), indicative of exciton emission rather than excimer emission.[10]

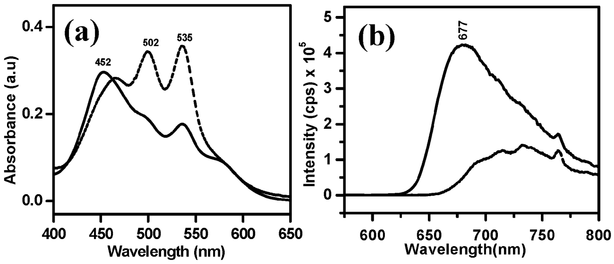

Fig. 2 (a) UV-Vis spectra of PI solution and loose gel of PI/MM at room temperature (solid lines for gel and dashed lines for PI solution). Typical molar ratio = 1 : 2, [PI] = 2.5×10^{-4} M and [MM] = 5×10^{-4} M [pathlength = 1.0 mm], (b) fluorescence spectra of solution and gel at room temperature of the PI system. Typical molar ratio = 1 : 2, [PI] = 1×10^{-2} M and [MM] = 2×10^{-2} M, at λ_{ex} = 475 nm [pathlength = 10 mm].

^{1}H-NMR titration studies (Fig. S8, ESI†) of PI with gradual addition of MM reveal an upfield shift of both types of protons of PI (H^a and H^b stand for the protons on the perylene core and the benzene moiety, respectively).[13] The extent of upfield shift of H^b (8.18 ppm to 8.01 ppm) is much higher than that of H^a (7.15 ppm to 7.10 ppm), indicating the larger shielding of the benzene ring caused by interaction between carboxylic acid of PI and amino group of MM. The shift of C=O stretching to ~38 cm^{-1} lower frequency in FTIR studies (Fig. S9, ESI†) indicates the participation of the H-bond between PI and MM in the gel. XRD studies (Fig. S10, ESI†) of the dried gel show that the gel fibers are highly crystalline. A diffraction peak around 24.5° indicates a well-defined and compact π–π stacking of perylene cores at the distance of 3.6 Å in gel fiber.

To investigate the importance of the π–π stacking, we have synthesized PBI having bromine atoms at the bay position of the perylene core. Upon mixing at an appropriate molar ratio, PBI also forms hydrogel with MM (Fig. 1c), however, 10 hours at room temperature are required to gelate water and a highly entangled network of PBI/MM fibrils is observed. For PBI gels, spectral studies (Fig. S11–S14, ESI†) also confirm the defined aggregation in the presence of two molar

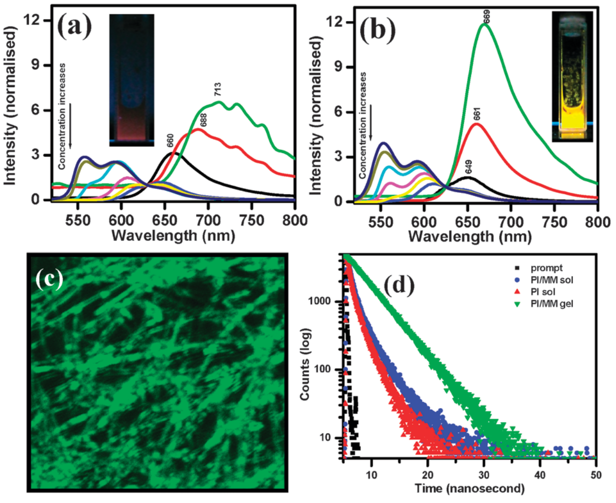

Fig. 3 Concentration-dependent fluorescence spectra of (a) PI only and (b) [PI]/[MM] = 1 : 2 solution in water at room temperature ([PI] = 3.75×10^{-5} (navy) to 3.75×10^{-3} M (green) and λ_{ex} = 475 nm). Arrows indicate spectral change upon increasing the concentration of PI [inset: PI only and fluorescent PI/MM hydrogels under UV irradiation at 365 nm]. (c) CLSM image of hydrogel of 1 : 2. (d) Time-resolved fluorescence decay of PI solution (red), PI/MM solution (blue) and PI/MM hydrogel (green) at 25 °C (λ_{ex} = 440 nm). The sharp profile on the left is the lamp profile (black).

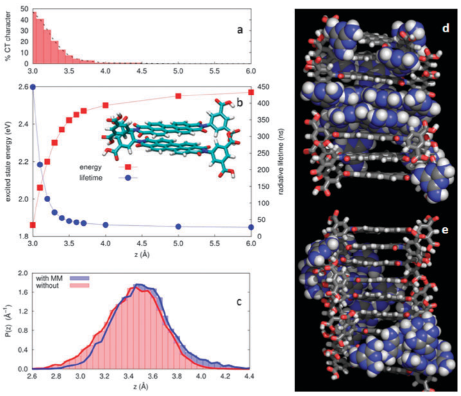

Fig. 4 (a and b) Charge-transfer character, electronic excitation energy and radiative lifetime for PI dimers *versus* the intermolecular spacing *z*, as calculated at the INDO/SCI level. (c) Simulated distribution of the intermolecular spacing for a couple of oppositely charged PIs inside a stack, in the presence and absence of MM. (d and e) Two MD snapshots showing the intercalation and the wrapping of MM around a PI stack.

equivalents of MM. Interestingly, the emission intensity of PBI/MM gel is less than that of PI/MM gel. Assuming limited heavy atom effects, it may be reasoned that the bay substituents significantly reduce π–π interaction as evidenced from XRD results (broadening of reflection at 24.5°, Fig. S10b, ESI†).

To understand why these fibers remain fluorescent in water, extensive molecular dynamics and simulations have been performed and MM stabilizes the assemblies of PI molecules into columns by gluing these together into a gel-like structure. Here, the presence of the phenyl rings bearing the carboxylic units at the N-terminal sites freezes the rotation angle (~30°) in both ground-state and excited-state potentials, so that the intermolecular distance is the main geometric factor prompting the formation of excimers as evidenced from the concentration dependence studies of PI (Fig. 3a). INDO/SCI and TD-DFT calculations of PI dimers extracted from MD simulations of the columns where the distance between the molecular backbones has been gradually reduced from 6 Å down to 3 Å (Fig. 4a and b) show an abrupt decrease in the lowest excitation energy, increase in the associated radiative lifetime and in the excited-state charge-transfer character at distances shorter than ~3.4 Å, which are all signatures of excimer emission.[14]

The addition of MM affects the packing of the PI molecules within the columns in multiple ways which have dramatic impact on the luminescent properties of the gels. MD studies reveal that MM molecules can be inserted into the columns (Fig. 4d), thus not only preventing direct quantum-mechanical coupling between PI molecules and hence excimer formation but also slowing down energy migration to weakly emissive excimer sites. Most importantly, MM molecules form a continuous belt of H-bonds cross-linking the PI stacks and preventing close contacts (below ~3.3 Å) between adjacent PI molecules in the excited state (Fig. 4c–e) (the excited-state potential is modeled here by adding partial charges on adjacent PI cores to mimic possible excimer formation).[10] As a result, exciton emission (optically allowed as a result of the finite angle between neighboring molecular transition dipoles and energetic/positional disorder along the columns) is favored over excimer emission (necessitating short intermolecular distances) in the presence of MM (seen in Fig. 3b).

In conclusion, we report the first example of perylene based hydrogels formed spontaneously upon mixing of a simple perylene diimide derivative with melamine. These gels exhibit highly intense fluorescence visible to the naked eye. The resulting gel network consists of inner core of H-stacked perylenes cross-linked by MMs and a water soluble carboxylic acid at the outer surface. The observation that the perylene derivative forms gel in aqueous medium is novel and will encourage the design of perylene based gelators aiming for a biological environment.

PKS is indebted to CSIR, India, for his fellowship. We acknowledge Dr A. Bandyopadhyay of IICB for CLSM. SM thanks Prof. A. K. Nandi of PSU, IACS, for his valuable suggestion and EU for MC Fellowship (fp7-people-2007-4-2-iif). The work was supported by the START-UP fund provided by IACS. AER thanks NWO, VICI and EU ITN Superior.

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