ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 1467–1469

www.rsc.org/chemcomm

COMMUNICATION

Fluorescent coronene monoimide gels *via* H-bonding induced frustrated dipolar assembly†‡

Ankit Jain, K. Venkata Rao, Chidambar Kulkarni, Anjana George and Subi J. George*

Received 11th August 2011, Accepted 16th September 2011
DOI: 10.1039/c1cc14990c

Two stage self-assembly of novel coronene monoimide (CMI) based gels that results in resurfacing of monomer emission in the aggregated state is reported. This process is attributed to a frustrated head–head dipolar assembly forced by hydrogen bonding.

Self-assembly of π-conjugated systems has resulted in immense amount of research involving insights into the supramolecular organization behaviors of molecules.[1] Systematic and engineered self-assembly of molecules with optical and electronic functionality has led to the evolution of various assemblies, such as π-conjugated organogels[2] with potential applications in organic electronics. However invariably, aggregation results in hampering of fluorescence of these molecules, which in most cases is an undesirable trait for their light-emitting properties.[3] Various schemes of emission enhancement as a result of aggregation have been probed, excimer emission,[4] exciplex emission,[5] energy transfer,[6] aggregation induced emission,[7] aggregation induced enhanced emission[8] to name a few. However still search for a novel methodology for enhanced emission during aggregation persists. On the other hand, controlling the self-assembly of dipolar dyes to parallel head–head organization has been a topic of great research interest because of their potential application in non-linear optics.[9]

Herein we report a novel approach to achieve fluorescent assemblies through hydrogen bonding mediated supramolecular polymerization of dipolar chromophores using the concept of repulsion between dipoles as they are forced into a head–head staggered organization. For this purpose we studied the self-assembly of unsymmetrical coronene monoimide (CMI) derivatives and the critical effect of its molecular dipole on the stacking interactions.[10] High emission characteristics of self-assemblies which could be translated in an organogel phase make this first CMI based gelator unique in its design and properties.[11] Further probing spectroscopically, their anomalous organization behavior, we inferred that monomer emission resurfaces as a supramolecular polymer stage is achieved.[12]

The dipolar chromophores, **CMI–ACH** and **CMI–CH** (Fig. 1a), have been designed with alkoxy substituted gallic amide groups, which would promote co-operative and synchronous functioning of H-bonding and π–π interactions.[13] **CMI–CH** consists of (*S*)-3,7 dimethyloctyloxy chiral chains in the gallic wedge and would provide a chiro-optical handle to probe the molecular organization and self-assembly characteristics. The CMI derivatives were synthesized according to literature procedures (Fig. S1, ESI‡) and characterized by various spectroscopic techniques such as ^{1}H-NMR and MALDI-TOF MS.

In toluene, the compound self-assembles to the extent that **CMI–CH** immobilizes toluene at a critical gelator concentration of 2.3 mM. **CMI–ACH** however does not form an organogel, but results in the formation of a viscous solution (2.5 mM), suggesting self-assembly. Morphological characteristics visualized through Field Emission Scanning Electron Microscopy (FE-SEM) and Atomic Force Microscopy (AFM) of both CMI derivatives showed the formation of a fibrous mesh of high aspect ratio with minimum width of an individual fiber being 5–6 nm (Fig. 1b and S2 (ESI‡)). IR spectra of the **CMI–CH** xerogel from toluene showed a lower energy amide band (3283 cm^{-1}) compared to the dried film from chloroform

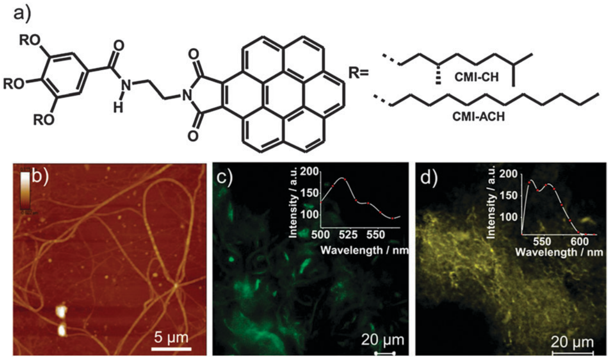

Fig. 1 (a) Molecular structures of **CMI–CH** and **CMI–ACH**. (b) AFM height image of **CMI–CH** fibers (2.5 mM, toluene) on a glass substrate. (c) and (d) Confocal microscopy images of **CMI–CH** in toluene and MCH respectively. Insets show the corresponding fiber emission spectra.

Supramolecular Chemistry Laboratory, New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, India-560064. E-mail: george@jncasr.ac.in; Fax: +91 80 22082627; Tel: +91 80 22082964

† This article is part of the *ChemComm* 'Emerging Investigators 2012' themed issue

‡ Electronic supplementary information (ESI) available: Experimental procedures, additional morphological and spectroscopic data. See DOI: 10.1039/c1cc14990c

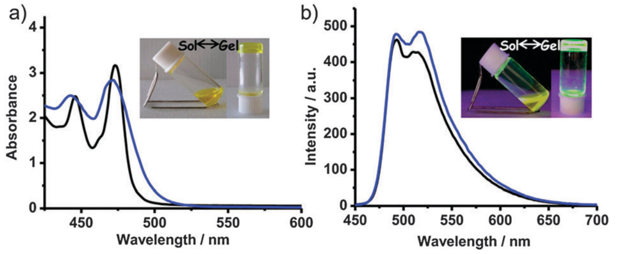

Fig. 2 Temperature dependent (blue = 90 °C, black = 20 °C) (a) UV-Vis spectra (2.5 mM) and (b) emission spectra (1.5 mM) of **CMI–CH** in toluene (l = 1 mm, front face geometry, λ_{exc} = 400 nm). Insets show the photographs of **CMI–CH** in solution and gel under visible and UV light respectively.

(3402 cm^{-1}) (Fig. S3, ESI‡) showing the presence of H-bonding in the self-assembly. Visualization of **CMI–CH** gel fibers through confocal microscopy showed that the self-assembled fibers in toluene and methyl cyclohexane (MCH) exhibit green and yellow fluorescence, respectively (Fig. 1c and d).[14]

Temperature dependent absorption spectra of toluene gel (2.5 mM) showed that the solution state is more broadened compared to the gel state (Fig. 2a) (see the ESI‡). Simultaneously, comparison of fluorescence spectra of the gel state with that of the solution state showed the high fluorescent nature (less than 5% quenching) of self-assembly, with mere changes in the vibronic features between the two (Fig. 2b). These observations suggest that CMI chromophores experience a monomer like environment as adjacent π clouds are interacting minimally to each other in the gel phase,[12] much contrary to the conventional π–π induced aggregation features. To get an insight into chromophore orientations during the self-assembly we first carried out concentration and temperature dependent NMR studies. Temperature dependent ^{1}H-NMR of 2 mM **CMI–CH** in toluene-d_8 showed upfield shifts in H_1 (coronene ring protons adjacent to the imide ring, Fig. S4, ESI‡) protons of the coronene ring when cooled from 60 °C onwards, possibly because of the shielding by the ring current of the adjacent aromatic rings. However, interestingly as the temperature decreased beyond 30 °C, as the molecule gelates toluene, H_1 proton shows a downfield shift suggesting the change in the environment around it, possibly because of a conformation change which results in deshielding. Concentration dependent ^{1}H-NMR studies of **CMI–CH** (0.01 mM to 5 mM) showed upfield shifts of H_1 proton as the concentration is increased up to 1 mM and a downfield shift started as the concentration was further increased to 5 mM, which is consistent with the transition observed in temperature dependent studies (Fig. S4, ESI‡). Above data clearly hint towards a two stage assembly process for **CMI–CH**.[15]

However, the UV and PL studies were unable to provide enough translation of the two stage aggregation process of **CMI–CH**. In addition, the toluene absorption in the 250–300 nm, where the gallic part of the molecule absorbs and the contribution of linear dichroism (LD) in the gel state, prevented the use of chiro-optical properties to follow the self-assembly. To probe the matter further we performed temperature dependent circular dichroism studies of **CMI–CH** in MCH. Although, **CMI–CH** is not soluble enough in MCH at higher concentrations to form gels, it self-assembles to form fibers at concentrations as low as 2 × 10^{-5} M and hence the aggregation studies could be performed at much lower concentrations (0.05 mM) compared to that in toluene. In a temperature drive from 60 °C to 20 °C ($dT/dt = -10$ °C min^{-1}) (Fig. 3), as the molecule aggregates, at low temperatures we found that only the gallic part is bisignated and not the CMI moiety (beyond 350 nm), suggesting that though chirality from chiral side chains has been transferred to chromophoric assembly, the adjacent chromophores are not excitonically coupled. This hints towards an anomalous disorientation among the adjacent π-clouds of CMI moieties as the molecule aggregates.

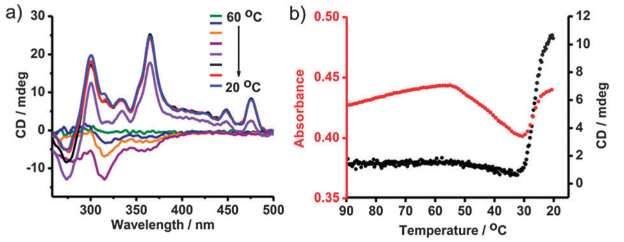

Fig. 3 (a) Temperature dependent CD spectra of 0.05 mM **CMI–CH** in MCH. (b) Temperature dependent absorption (red) and CD (black) cooling curves ($dT/dt = -10$ °C min^{-1}) for 0.05 mM **CMI–CH** in MCH monitored at 476 nm (l = 1 mm, front face geometry).

Moreover, the temperature dependent CD studies also provided evidence of a two stage self-assembly process. Carefully, analyzing the CD spectra we found that as the temperature is decreased from 60 °C to 20 °C, the initial molecularly dissolved state and the final aggregated state have a reverse chirality transition state in between. Temperature dependent absorption and CD traces followed at 476 nm unambiguously show two states, first being in between 54 °C and 36 °C, resulting in decrease of absorbance and the second in between 36 °C and 20 °C resulting in increased absorption (Fig. 3b). These observations point towards a supramolecular conformational change during the process of aggregation. Since the design of our system is not symmetric across the coronene ring there must be a component of the residual dipole moment of the CMI moiety in the plane of the molecule. From the above observations we believe that the first transition from the molecularly dissolved state corresponds to dipolar head–tail π–π stacking interactions to satisfy the dipolar interactions, which is evident from the decrease in absorption, upfield shifts in H_1 proton signal and the negative Cotton effect which is not bisignated at both gallic and CMI absorptions. However, when H-bonding interactions set in at lower temperatures (signified from the appearance of positive bisignated Cotton effect in the gallic region, Fig. 3), maximum π–π overlap means CMI dipoles would be in an energy intensive head-to-head organization and thus would be forced to reduce the π cloud overlap to cope up with the dipolar repulsion. This results in a frustrated assembly of distorted chromophores, which is a compromise between the attractive π–π interactions and repulsive dipolar interactions. This second transition is evident from the downfield shifts in the aromatic protons and the reversal of the Cotton effect with a positively bisignated CD signal for the gallic moiety and a non-excitonically coupled positive Cotton effect for CMI. The spectroscopic changes observed made us visualize CMI assemblies as a linear chain

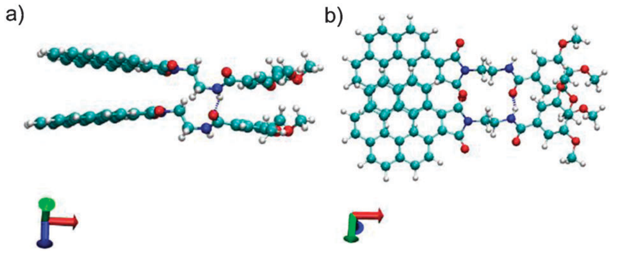

Fig. 4 Optimised conformations of the CMI dimer: (a) lateral and (b) top view.

supramolecular polymer with frustrated pendant assembly of dipolar CMI moieties (Fig. S5, ESI‡). Thus, giving the notion of least π–π interaction during the maximum H-bonding state, as evident from the above temperature dependent studies. To affirm the facts even further, to a toluene gel of **CMI–CH** (2 mM, 1 mm cuvette) we added 1 μl of trifluroacetic acid which resulted in disruption of H-bonding and thus breaking the gel. Physically the color of the solution darkened and fluorescence quenched suggesting towards a π–π interaction driven self-assembly only when H-bonding interactions are not operative (Fig. S6, ESI‡).

To probe the validity of our dipolar interaction based hypothesis which leads to such an anomalous behavior in CMI self-assembly, we optimised the model structures to provide insights into the molecular packing. The dipole moment of the CMI chromophores were calculated to be 3.86 D, which results from the unsymmetrical substitution at the coronene ring, which is consistent with our expectations. Further calculations on an optimised dimer showed that indeed due to the CMI residual dipole the adjacent coronene surfaces in an aggregate are skewed and the distance between them is of the range greater than 4 Å thus resulting in a very weak π–π interaction if there is any (Fig. 4 and S7, ESI‡). The dimers concomitantly had a strong H-bonding between adjacent amide bonds. The theoretical calculations thus affirm positively our hypothesis explaining the anomalous photo-physical behavior of CMI aggregates.

In conclusion, we have synthesized and elucidated the self-assembly properties of novel coronene monoimide derivatives. Detailed analytical probing revealed subtle molecular changes that governed the spectroscopic properties of the aggregates. Moreover it is one of the few examples where disjunction between two usually complimenting forces, π overlap and H bonds, has been shown. More importantly, the concept of chromophore disorientation upon H-bonding enforcement, a consequence of minimizing dipolar repulsion, if generalized to other chromophores whose quantum yield decreases on aggregation, can be of great significance. Moreover an arrangement that forces the dipole to aggregate in a head–head fashion can be advantageous for NLO activities. Though much work on these applications needs to be explored, this study provides a base for molecular understanding for such future directions.

We thank JNCASR and Department of Science and Technology (DST), Government of India, for financial support. K.V.R thanks CSIR for scholarship. The authors acknowledge Prof. E. W. Meijer for stimulating discussions, Prof. S. Balasubramanian for the computational facilities, Prof. G. U. Kulkarni for Veeco-lab facilities, and Basavraj (AFM), Selvi (FE-SEM), and Suma (confocal) for measurements.

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