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Chemical Communications

## Three Component Assembly by Orthogonal H-Bonding and Donor-Acceptor Charge-Transfer Interaction

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Received ooth January 2012, Accepted ooth January 2012

Cite this: DOI: 10.1039/xoxxooooox

DOI: 10.1039/x0xx00000x

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Three component supramolecular assemblies from a mixture of an aromatic donor (D), acceptor (A) and external structure directing agent (ESDA) is achieved by orthogonal noncovalent interactions involving two different types of Hbonding and alternate D-A stacking. ESDA containing amide or urea produces charge-transfer gel and sol, respectively, owing to their contrasting morphology.

Elegant functions performed with ultimate perfection by biological self-assembled systems provide the inspiration to study supramolecular assemblies of abiotic units <sup>1</sup> and explore their utility <sup>2</sup> in diverse applications including biology <sup>3</sup> and material science. Their diversity in terms of structure and function increases exponentially with growing number of different building blocks integrated in a single system by non-covalent forces. While there exists many examples of two component assemblies,<sup>5</sup> three component assemblies remain scarce.<sup>6</sup> In the recent past we have shown that an external structure directing agent (ESDA) can induce gelation of a naphthalene-diimide (NDI) building block by orthogonal H-bonding.<sup>7</sup> To explore this supramolecular design further, we have taken one step forward and examined co-assembly of an aromatic donor (D) and acceptor (A) chromophore in presence of a suitable ESDA (Scheme 1) by D-A charge-transfer (CT) interaction <sup>8-10</sup> and two different types of H-bonding operating simultaneously in orthogonal directions.<sup>11</sup>

NDI-1 (A) and Py-1 (D) contain a carboxylic acid group that is complementary to the pyridine group of the ESDA. The ESDA also contains an amide or urea for concurrent H-bonding in orthogonal direction. Three component assemblies were tested with NDI-1 + Py-1 + ESDA-A (1:1:2) in methyl cyclohexane (MCH) while macroscopic precipitation was noticed. However, in presence of 10 % CHCl<sub>3</sub> the mixture produces a homogeneous yellowish solution upon heating which at rt transforms to a red transparent gel (Fig 1) suggesting alternate D-A stacking.  $T_g$  was estimated to be 31°C (c =10 mM) suggesting weak nature of the gel which was also reflected in very low yield stress value (0.3 Pa at c = 12 mM) that was obtained from the rheological measurements (Fig S1). As a control, few other combinations such as (NDI-1 + ESDA-A), (NDI-1 + Py + ESDA-A), (NDI-2 + Py + ESDA-A), (NDI-2 + Py-1 + ESDA-A) and (Py-1 + ESDA-A) were tested while none found suitable (Fig

S2) for gelation suggesting necessity of both CT-interaction and orthogonal H-bonding for gel formation.



Scheme 1: Top-Structure of donor-acceptor building blocks and ESDA; Bottom- Schematic showing three-component assembly

Gelation was also attempted in few other nonpolar organic solvents with varying D: A ratio but no other combination except1:1 D/ A in MCH/ CHCl<sub>3</sub> (90/ 10) produced gel (Fig S3). This indirectly suggests alternate D-A sequence rather than random distribution of the two units as in that case 1:1 stoichiometry may not be prerequisite for gelation. Trace amount of a protic solvent MeOH destroys the gel with concomitant disappearance of the color (Fig 1a) confirming H-bonding is the cause while D-A stacking is the consequence. This is also confirmed by UV/vis spectra (Fig 1a) which shows drastically reduced CT-band in presence of MeOH (for solvent dependent UV/vis spectra see Fig S4). To elucidate the molecular arrangements in the gel state, powder XRD studies were carried out with the xerogel (Fig 1b). Intense and sharp reflection is seen in the low angle that corresponds to d = 46.6 Å along with relatively less intense peaks for d/2 (23 Å), d/3 (11.6 Å) and d/4 (7.9 Å) indicating lamellar organization. The observed d spacing of 46.6 Å corroborates well with the summation (52.03 Å) of simulated lengths of ESDA-A and NDI-1 (for energy minimized structures see Fig S5) supporting the proposed mode of co-assembly (Scheme 1). To gain more insight into the inter-molecular interactions, <sup>1</sup>H NMR of the gel was compared with those of the individual components

(Fig 1c). Notably the amide proton ( $H_b$ ) of the ESDA-A is downfield shifted by ~ 0.5 ppm suggesting it is involved in H-bonding.



Fig 1: a) Selected region of UV/vis absorption spectra of the gel produced by {NDI-1 (2.5 mM) + Py-1 (2.5 mM) + ESDA-A (5.0 mM)} in MCH/ CHCl<sub>3</sub> (90: 10) and its fate after MeOH addition. Inset shows images of the corresponding samples. b) Powder XRD data of the xerogel; c) <sup>1</sup>H NMR spectra (selected region) of the gel (in CDCl<sub>3</sub>/ MCH = 10: 90) and individual components (in CDCl<sub>3</sub>).

The H<sub>d</sub> proton that is adjacent to the nitrogen atom of the pyridine ring is also downfield shifted possibly due to the generation of  $\delta$ + charge on the N atom in the H-bonded state. Furthermore the NDI ring protons (H<sub>a</sub>) experience most prominent upfield shift in gel state compared to sol as a result of shielding effect in the alternate D-A stacking. Same is also true for the pyrene ring protons although to a lesser extent which is consistent with previous reports on alternate D-A stacking.<sup>12</sup> A comparison of the FT-IR spectra of the gel with those of the individual components (Fig S6) further supports the Hbonded three component assembly (Scheme 1) although detail analysis was not possible due coincidental overlap of several peaks. Further we examined ESDA-U (Scheme 1) which differs with ESDA-A only in the urea functionality instead of amide. NDI-1 + Py-1 + ESDA-U (1:1:2) in MCH/ CHCl<sub>3</sub> (90: 10) also shows intense red color (inset-Fig 2a) indicating CT-complexation. But to our surprise, no gelation was observed even for samples with tenfold higher concentration. To examine the inter-component interactions we studied self-assembly in this case also by <sup>1</sup>H NMR as in case of ESDA-A (Fig 1c) and noticed (Fig S7) similar behavior indicating existence of H-bonding and D-A alternate stacking. To understand possible reasons for lack of gelation ability for ESDA-U, we compared the association constants (K) for the CT-complex in presence of this two different structure directing agents by concentration dependent UV/ vis experiments (Fig S8, S9).<sup>13</sup> The K values were estimated to be 42 (extinction coefficient of the CTband =3.77 x  $10^3$  M<sup>-1</sup>cm<sup>-1</sup>) and 98 M<sup>-1</sup> (extinction coefficient of the CT-band = 1.96 x 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) for ESDA-A and ESDA-U, respectively,<sup>14</sup> suggesting actually better assembly in case of the urea containing ESDA. Further their thermal stabilities were compared by variable temperature UV/vis (Fig 2a, 2b). With increasing temperature, the CT-band gradually decreases in linear fashion in both cases suggesting disassembly and lack of any cooperative nature. To have a comparison, the respective  $\alpha_{agg}(T)$  (mole fraction of aggregate at temperature T) values were estimated (see supporting information for detail). A plot of  $\alpha_{agg}$  vs. T (Fig 2c) indicates stiffer slope for ESDA-A suggesting lower stability.



**Fig 2**: Variable temperature UV/vis spectra of the three component assembly in presence of (a) ESDA-A and (b) ESDA-U; (c) Plot of  $\Box_{agg}$  Vs Temperature; inset in (a)- image of the CT-sol of NDI-1 (2.5 mM) + Py-1 (2.5 mM) + ESDA-U (5.0 mM) in MCH / CHCl<sub>3</sub> (90: 10).

Notably Fig 2a indicates appearance of the CT-band prior to the gelation ( $T_g = 31$  °C) indicating D-A complexation actually induced gelation. This was also confirmed by cursory observation (Fig S10) where we noticed red coloration even before gelation, upon cooling of a three component mixture. This raised the question on the sequence of different interactions involved in the gelation. To gain better insight we examined the FT-IR spectra of the ESDA-A alone which showed (Fig S11) existence of H-bonded amide groups even at elevated temperature where the CT-band diminishes. This indicates that the ESDA-A self-assembles first to produce a multivalent receptor which facilitates the D and A components to assemble in alternate fashion and only beyond a certain threshold of the D-A complexation (which is achieved at the  $T_{g}$ ) the selfassembly leads to gelation. However, this does not explain the lack of gelation for ESDA-U containing three component system. Thus to understand the reason for anomalous gelation property, we checked their morphology. TEM images (Fig 3) of NDI-1 + Py-1 + ESDA-A shows fibrillar morphology that is typical for a gelator. In contrary NDI-1 + Py-1 + ESDA-U combination produces ill defined particles with diameter less than 10 nm which was also supported by dynamic light scattering (DLS) measurements revealing (Fig S12) presence of aggregates with  $D_{\rm h} < 10$  nm. Further we examined the effect of D/ A ratio [(D + A) = ESDA-U] and observed gel formation (Fig S13) only at D: A = 1: 3 unlike the red solution at D: A = 1: 1. TEM images of the diluted gel showed elongated fibres (Fig S14) and in DLS a peak appeared (Fig S14) corresponding to average hydrodynamic diameter of ~ 900 nm in sharp contrast to <10 nm for 1: 1 mixture. In absence of any donor the mixture resulted in macroscopic precipitation. Based on these results a possible model is shown in Fig 3.



**Fig 3**: Possible mode of assembly that leads to contrasting TEM morphology for three component organization in presence of ESDA-A (left) and ESDA-U (right).

In case of ESDA-U, the supramolecular polymerization grows with a curvature and thus produces ill defined tiny particles which can be compared to cyclic in conventional step growth polymerization. Noteworthy that in a previous report we showed urea-urea H-bonding with a longitudinal displacement which caused slipped assembly for the attached dialkoxynaphthalene chromophores.<sup>15</sup> But for alternate D-A assembly in the present system, face-to-face arrangement is possibly more favorable and thus to accommodate

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both these structural demands, the ESDA-U stacks with longitudinal as well as rotational displacement that leads to the formation of small particles. However, this curvature (arising out of rotational displacement) may not be essential in presence of excess acceptor as in that case there will be several segments containing A-A sequence which is anyway known to adopt a slipped stacking that is compatible with the H-bonding motif of urea. Thus elongated fibrillar morphology and gelation is noticed in case of 1: 3 D/ A. This also confirms absence of any other type of possible H-bonding (such as carboxylic acid-urea) in the mixture containing ESDA-U, because in that case varying stoichiometry of D/A would not have so drastic effect on morphology and gelation.

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#### Conclusions

We have shown an ESDA can co-assemble two different molecular entities in alternate fashion by orthogonal H-bonding and CT-interaction. Depending on the nature of H-bonding functionality in the ESDA, either a 1D fibre or particles are formed resulting in gel or sol, respectively. This is related to the differences in the spatial organization of the alternately stacked D and A units as per the constraint imposed by the H-bonding motif of the particular ESDA. CT-complexes have received renewed interest in the recent past due to emerging reports on their ferroelectric properties<sup>16</sup> and high mobility in field effect transistors.<sup>17</sup> Present findings are highly relevant in those contexts considering the unique supramolecular design which offers opportunities for plenty of structural manipulation in the ESDA for tuning the co-assembly properties.

#### Notes and references

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<sup>†</sup> We thank Mr. M. R. Molla for providing NDI-1. HK thanks CSIR for a research fellowship. SG thanks SERB for funding (SR/S1/OC-18/2012).

Electronic Supplementary Information (ESI) available: [Synthesis and characterization, materials, methodology of all experiments and additional spectral data]. See DOI: 10.1039/c000000x/

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### Three Component Assembly by Orthogonal H-Bonding and Donor-Acceptor Charge-Transfer Interaction

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