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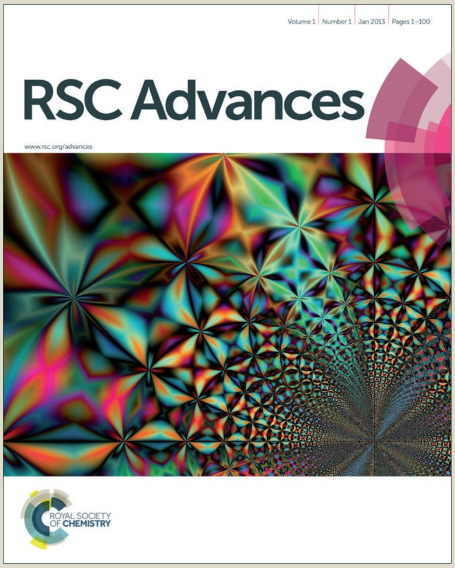
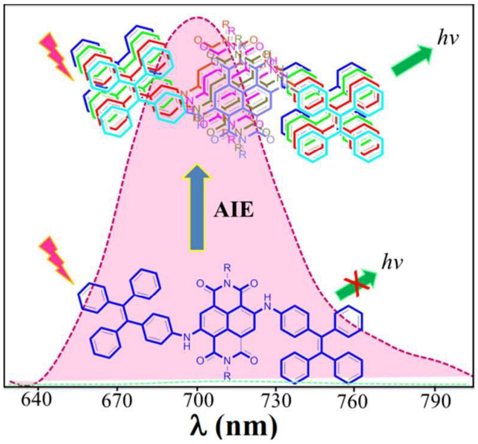


Graphical Abstract



Tuning non-emissive NDIs into highly fluorescent material in aggregated by employing AIE-active tetraphenylethylene to the core *via* ICT effect.

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Solvophobic control aggregation-induced emission of tetraphenylethene-substituted naphthalene diimide *via* intramolecular charge transfer†

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Two new tetraphenylethene-core-substituted naphthalene diimide (TPE-cNDI) were synthesized through linking one and two TPE, where TPE acts both as an electron-donor for ICT and also display characteristic of AIE effect i.e. non-emissive in solution but enhanced red-emission in both the aggregated and the solid state with high quantum efficiency. Furthermore, both the derivatives self-assembled into variety of nano- to micro-structures *via* solvophobic control.

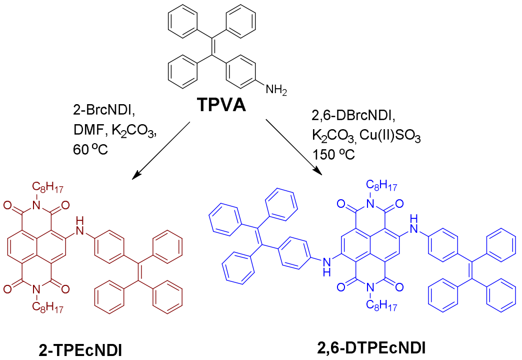
Among aromatic molecules that have found utility, particularly in the design of mechanochromic luminescent materials, the tetraphenylethylene (TPE) molecules have attracted much attention due to their tendency to be non-emissive in the dissolved state but enhanced emission can be seen in both the aggregated form and the solid state.[1] This phenomenon is so–called "aggregation-induced emission" (AIE)[2] and aggregation-induced enhanced emission (AIEE).[3] Since then, TPE derivatives have been used for supramolecular building blocks,[4] fluorescence ''turn on'' chemosensors for selective detection of Ag^+ and Hg^{2+} ions[5] and acid/base sensing in solution and living cells[6]. Inspired from this, we have shown that TPE-based porphyrin for formation of nano- to micro-ring structures similar to light harvesting antenna.[7]

In recent years, core-substituted naphthalene diimides (cNDIs) have gained wider attention than unsubstituted NDIs due to their electro-optical properties and applications in organic, supramolecular, medicine, material sciences and organic electronics.[8] cNDIs are a smaller version of previously used π-conjugated polycyclic aromatic compounds, which can be functionalised *via* core substitution.[9,10] Such NDI derivatives have been widely used in investigating organic dyes that have found promising applications for use as active components in organic light harvesting systems,[11] n-type channel field effect transistors.[12] Although cNDI has shown to be very attractive component as they demonstrate varying near-unity fluorescence (FL) quantum yield in dilute solution. However, they suffer drawbacks due to aggregation caused quenching (ACQ)[13] in aggregates and solid state due to the attractive dipole–dipole interactions and/or effective intermolecular π–π-stacking and cannot be used as is for mechanochromic luminescent material.

Synthesising cNDI-based NDI dyes that efficiently emit in the solid and also aggregated state is of interest. Recently, Tang group showed that the substitution of perylene diimides (PDIs) through imide or bay position resulting PBIs exhibit desirable quantum efficiency in light emission.[14] In other examples, Zhu[15a,b] and Tang[15c] groups have shown that when donor-acceptor functionalised with TPE moieties used, in which TPE acts both as an electron donor for intramolecular charge transfer (ICT)[15d] as well as activator for AIE.[15a-c]

Based on these results, and our understanding in cNDI field, it is a rational assumption to tackle notorious ACQ effect of cNDIs by core-substitution with TPE moieties which is both with electron-donor for ICT and activator for AIE because (1) cNDI is smaller analogue of PDIs, whether AIE effect will observe by linking TPE through core of NDIs, and (2) it is an important to know the effects of attaching twisted TPE moieties onto the NDI core for the assembling behaviour as well as ICT effect in varying solvent polarity.

In this report, we describe synthesis of two new (2-TPEcNDI and 2,6-DTPEcNDI) core-substituted NDIs bearing one or two amino-TPE functionality at the core (Fig. 1), and study their AIE ICT effect upon aggregation *via* solvophobic control.



Scheme 1. Synthesis of TPE-substituted naphthalene diimides (2-TPEcNDI and 2,6-DTPEcNDI).

Synthesis of intermediate of 4-(1,2,2-triphenylvinyl)aniline (TPVA), 2-BrNDI[9] and 2,6-DBrcNDI[9] described detail in the Electronic Supplementary Information (ESI).† The 2-TPEcNDI and 2,6-DTPEcNDI was prepared reacting 2-BrcNDI with TPVA in the presence of K_2CO_3 as a base in dry DMF at 70 °C, yielded 2-TPEcNDI (red compound) in 61%. However, similar condition failed to produce 2,6-DTPEcNDI by reacting 2,6-DBrcNDI with TPVA. The 2,6-DTPEcNDI was synthesised grinding and heating mixture of 2,6-DBrcNDI, TPVA (3 equiv.) and K_2CO_3 (6 equiv.) in the presence of Cu(II)SO_3 (6 equiv.) at 150 °C for 2 d, gives blue compound with yield of 55%. Both the derivatives 2-TPEcNDI, 2,6-DTPEcNDI was purified by column chromatography using silica gel by eluting with CH_2Cl_2. The 2-TPEcNDI and 2,6-DTPEcNDI derivatives are well soluble in common organic solvents such as tetrahydrofuran (THF), chloroform ($CHCl_3$), however, they display poor solubility in hexane and polar solvents such as methanol and water.

The UV-vis absorption spectra of 2-TPEcNDI and 2,6-DTPEcNDI in $CHCl_3$ shows a structured band with a maximum at 519 and 629 nm, respectively, which is typical for the S_0-S_1 transition of the isolated NDI chromophore (Fig. 1a). The second absorption band (300–400 nm) with peak maximum at 319 and 349 nm, respectively, is due to a π–π* transition involving both the NDI and TPE units. The results demonstrate that the electron-donating TPE substituent introduced to the naphthalene core affects the electronic structure of NDI in a similar fashion to 2,6- or 2,3,6,7-core-substitution.[16]

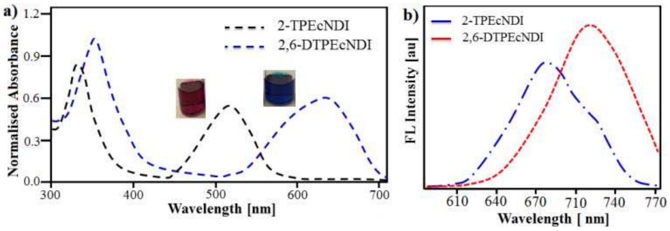


Fig. 1 (a) UV-vis absorption spectra of TPE-core-substituted naphthalene diimide dyads (2-TPEcNDI and 2,6-DTPEcNDI) in $CHCl_3$, concentration of solutes: 10^{-5} M and (b) solid state fluorescence (FL) upon excitation wavelength: 629 and 519 nm, respectively. Inset in (a) is respective color of the compounds in $CHCl_3$.

The fluorescence (FL) of 2-TPEcNDI (10^{-5} M) in cast film shows a peak at 679 nm with a fluorescence quantum yield (Φ_f) 6.9 %, which is higher than Φ_F in $CHCl_3$ and THF i.e. 1.9%, 0.9% respectively. The fluorescence quantum efficiency (Φ_F) of the samples with absorption (intensity ~0.05) was estimated using fluorescein in ethanol (Φ_F = 70%) as standard solution and Φ_F of the solid films was measured using an integrating-sphere photometer. Interestingly, the di-TPE substituted cNDI (2,6-DTPEcNDI) shows quite different behaviour than 2-TPEcNDI. The emission of 2,6-DTPEcNDI shows the maximum peak intensity at near-IR region i.e. 717 nm (Fig. 1b) with Φ_F 18.3%, however, in $CHCl_3$ FL signals is to the noise level was detected with Φ_F = 0.09%.

Further the ICT effect within donor-acceptor systems is determined by solvent polarity using UV-vis absorption and photoluminescence (PL) spectroscopy (See ESI Table S1). The PL spectra of both the compounds 2-TPEcNDI (10^{-5} M) and 2,6-DTPEcNDI (10^{-5} M) shows solvent dependent emission ranging from 569 nm to 618 nm and 675 nm to 705 nm, respectively. The peak shifts in polar solvent are assigned to form the locally-excited state of TPE and the ICT state from TPE to NDI moieties, similar to donor-acceptor charge transfer in polar solvents.[15b,d] These results clearly shows that there is restricted intramolecular rotation of TPE moieties exhibit both AIE and ICT behaviour, which dissipate the excitation energy thereby weak emission for molecule 2,6-DTPEcNDI in dilute solution.[17] On the other hand, 2-TPEcNDI which has only one TPE moiety, thus the number of freely rotary phenyl group is the half of that in 2,6-DTPEcNDI.[14]

Furthermore, we investigated the AIE behaviours of 2-TPEcNDI and 2,6-DTPEcNDI in hexane/$CHCl_3$, methanol/$CHCl_3$ and water/THF with different volume percentage of hexane (f_h), methanol (f_m), and water (f_w), respectively. Typically, Fig. 2a shows the FL spectra of 2-TPEcNDI in hexane/$CHCl_3$, when $f_h < 60\%$, the green characteristic band appeared at 573 nm. However, increase of f_h percentage 60-80%, the emission is gradually enhanced. In f_h = 90%, the red band with Φ_F 12.8%. Similar AIE effect of 2-TPEcNDI in methanol/$CHCl_3$ mixtures gives Φ_F = 9.7%. Typically, the FL intensity gradually increases with increase f_m, and intensity decrease beyond 80%. This may be due to two important effect: first one is ICT effect and second is the hydrophobic nature 2-TPEcNDI molecules, which isolate when hydrophilic methanol is added by forming larger aggregates and precipitate quickly from solution, which decreases the number of the emissive species in the mixture.[14] In THF/water mixtures, the precipitate of 2-TPEcNDI quickly observed when only 40% water fraction was added and the lower fluorescence enhancement was observed compare to $CHCl_3$/hexane and $CHCl_3$/methanol systems (Fig. 3a). The calculated Φ_F in 40% water fractions gives 7.1% (Fig. 3b).

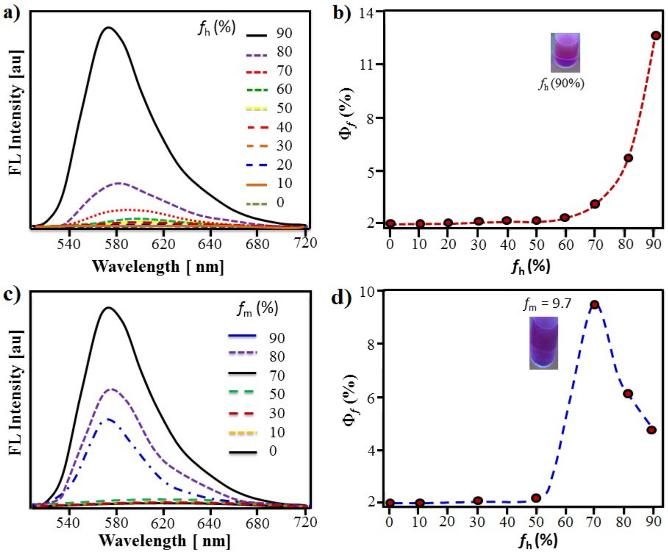


Fig. 2 The fluorescence (FL) spectra of 2-TPEcNDI (a) in $CHCl_3$/hexane mixtures with different f_h values. (b) The changes in Φ_F and λ_{em} with f_h. (c) FL spectra in $CHCl_3$/methanol mixtures with different f_m values. (d) The changes

in Φ_F and λ_{em} with f_m. The insets of (b) and (d) shows the photographs of the FL images of 2-TPEcNDI (10 μM; λ_{ex} = 365 nm) for the f_h = 90%.

The FL spectra of 2,6-DTPEcNDI clearly shows different features as compared to that of 2-TPEcNDI in hexane/$CHCl_3$. When f_h < 40%, no FL peak can be seen, however, f_h = 90%, a red band at 681 nm observed with Φ_F 21.9% (Fig. 3c and 3d). Since hexane is a non-polar solvent, containing enough hexane in the mixture would make the molecules self-assemble and aggregate in the mixture. This is true for AIE phenomenon, where 2,6-DTPEcNDI is well soluble in $CHCl_3$ solution, the active intermolecular rotations of the multiple phenyl rotors in TPE around the NDI consume the excited energy and quench the fluorescence. However, f_h = 90%, 2,6-DTPEcNDI aggregates *via* π–π-stacking which restricts the rotation of the phenyl rotors and induces the enhancement of emission of the fluorescence. The enhancement Φ_F of 2,6-DTPEcNDI was observed as compare to 2-TPEcNDI in THF/water (f_w = 40%) and $CHCl_3$/methanol (f_m = 70%) which is 15.3% and 19.1%, respectively (Fig. 4d). Such an observation clearly indicates that the hydrophobic 2-TPEcNDI and 2,6-DTPEcNDI molecules had formed large aggregates, as both water/THF are hydrophilic solvents and only those smaller ones in the suspension contributed to the emission. In later two solvents i.e. methanol/$CHCl_3$ and water/THF, the FL yield is not as high as that observed in the hexane/$CHCl_3$ system which is attributed the ICT behaviour to the electron-donating ability of TPE and the AIE behaviour to the restriction of intramolecular rotation of the TPE rotors in either polar or non-polar solvents.[15a-c] These results demonstrate the dual ability of TPE to induce AIE behaviour and behave as an electron-donor with higher fluorescence of donor-acceptor based material in aqueous media. Enhancement of fluorescence emission and shift is only due to the modification of cNDI with TPE moieties which transferred the emission from green to red, we can conclude that both the derivatives 2-TPEcNDI and 2,6-DTPEcNDI are typical AIE active molecules.[14]

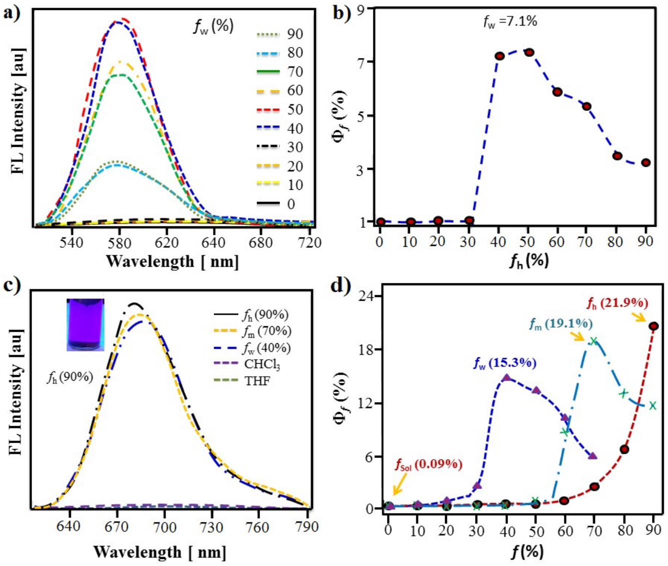


Fig. 3 (a) FL spectra of 2-TPEcNDI in THF/water mixtures with different f_w values. (b) The changes in Φ_F and λ_{em} with f_w. (c) FL spectra of 2,6-DTPEcNDI in $CHCl_3$, THF, $CHCl_3$/methanol, $CHCl_3$/hexane, THF/water mixtures with different f values. (d) The changes in Φ_F and λ_{em} with different fractions (f). The inset of (c) shows the photographs of the FL images of 2,6-DTPEcNDI (5 μM, λ_{ex} = 365 nm) from $CHCl_3$/hexane (f_h = 90%) mixture, respectively.

To understand mode of aggregation, we have performed UV-vis absorption spectra of 2-TPEcNDI in poor and good solvent such as $CHCl_3$, THF, hexane/$CHCl_3$ (f_h = 70%), methanol/$CHCl_3$ (f_m = 70%) and water/THF (f_w = 40%), respectively. Aggregation effect in which a reduction in the peak intensity and significant blue-shift of the absorption maximum along with loss of fine structure are seen in mixed good and poor solvents as compared to bands in THF and $CHCl_3$ alone (See ESI Fig. S1) and also the relative intensity of S_1–S_0 and S_0–S_1 bands reverse. These features suggest the formation of *J*-aggregation by arranging 2-TPEcNDI molecules in slipped face-to-face fashion.[18] These results prompted us to further investigate the aggregates around the point of aggregation using scanning electron microscopy (SEM).

It has been well documented that cNDI derivatives bearing alkyl chains, amino acids and oligoethylene chains does not interfere strong π–π–interaction between NDI cores are likely to assemble into ordered one-dimensional (1D) nanostructures such as wires, rods, vesicles, worm-like and belts-like nanostructures.[19] It is interesting to study whether bulky TPE substituents on the NDI core have an effect on the aromatic interactions and whether ordered structures can be formed. Interestingly, both the derivatives 2-TPEcNDI and 2,6-DTPEcNDI can be easily self-assembled into micrometre long microstructures in the mixtures of f_h, f_m and f_w as shown in Fig. 4.

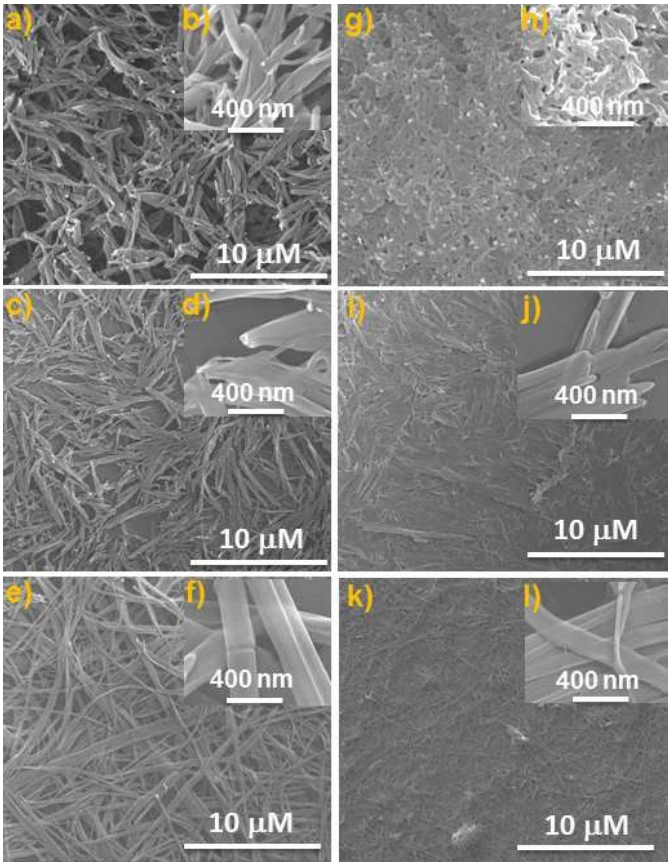


Fig. 4 (a–l): SEM images of the self-assembled aggregates formed by 2,6-DTPEcNDI and 2-TPEcNDI molecules in different conditions, respectively. (a, b, & g, h) in $CHCl_3$/methanol mixture with a methanol fraction (f_m = 70%), (c, d, & i, j) in $CHCl_3$/hexane (f_h = 90%) and (e, f & k, l) in THF/water mixture with a water fraction (f_w = 40%), respectively. In all the experiments, the concentration of 2,6-DTPEcNDI and 2-TPEcNDI used is 10^{-5} M.

Typically, SEM images of 2,6-DTPEcNDI in a mixture of $CHCl_3$/methanol (f_m = 70%) assembled into fibril structures with lengths of several tens of microns and diameters ranging from 50–200 nanometres (Fig. 4a and 4b). A crystalline rod-like microstructures with diameter of 100-300 nm from $CHCl_3$/hexane (f_h = 90%) was observed (Fig. 4c and 4d). In THF/water (f_w = 40%), 2,6-DTPEcNDI assembled into belt-like nanostructures with length of tens of micrometres (Fig. 4e) and width about 200-400 nm (Fig. 4f). Changing methanol, hexane or water concentration does not affect the morphologies (See SI Fig. S2-S6).

Conversely, 2-TPEcNDI in $CHCl_3$/methanol (f_m = 70%), self-assembled into elongated fibrils with several micrometres length (Fig. 4g, 4h). In $CHCl_3$/hexane (f_h = 90%), 2-TPEcNDI assembled, crystalline needle-like nanostructures with diameter ranging from 100-400 nm (Fig. 4i, 4j). Interestingly, elongated ribbons with diameter of 200 nm from THF/water (f_w = 40%), is observed (Fig. kh and 4l). Form this finding it is clear that bulkier TPE induced AIE effect on cNDI derivatives and does not interfere π–π–stacking between NDI cores rather the crystalline packing of terminal TPE moieties gives a unique design TPE through face-to-face stacking of the molecules with solvophobic control.

The morphology of the crystals aggregated from THF/water (f_w = 70%) were further investigated by transmission electron microscopy TEM (Figure 5a, 5b) and the crystallinity was characterized by XRD (Figure 5c). The morphology of obtained crystals is of structure of nanobelts with 100-400nm in diameter and 5 - 10 µm in length, which is consistent with the results from SEM images (Fig. 4e). Low angle XRD display the strongest sharp diffraction peaks at around 38^{o}C and 44^{o}C demonstrate that the resulted materials are highly crystalline (Figure 5c).[20]

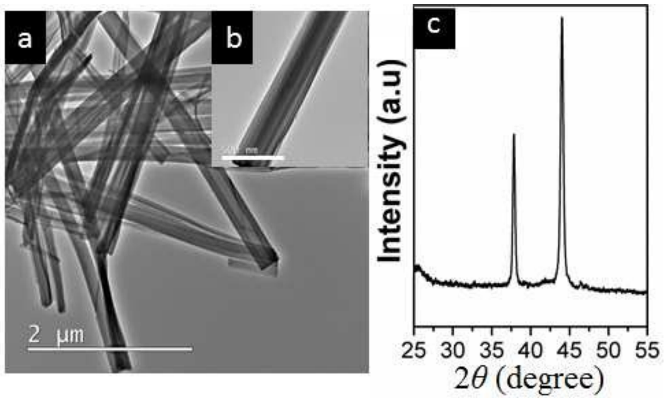


Figure 5: TEM and XRD images of the 2,6-DTPEcNDI in THF/water mixture with a water fraction (f_w = 70%), (a) low-magnification TEM image of an nano-belt structure (Scale bar = 2 µm), (b) high-magnification TEM image (Scale bar = 500 nm) and (c) powder X-ray diffraction patterns.

In summary, we described synthesis of two new mono- and di-TPE substituted NDI derivatives and studied comparative fluorescence behaviors, results clearly demonstrate that introduction of TPE functionality on to the core of NDI which demonstrated a conversion in the fluorescence performance of cNDIs from ACQ to AIE. Our findings also show that the modification of the cNDI with one TPE moiety can only partially alter the FL properties. Typically, the mono-TPE substituted NDI (2-TPEcNDI) in dilute $CHCl_3$ solution shows the characteristic FL features with decreased (Φ_F = 1.9%). Its aggregates formed in $CHCl_3$/hexane (f_h = 90%) and the powder sample emit red fluorescence ($\lambda_{em,solid}$ = 679 nm, $\lambda_{em,aggr}$ = 638 nm, Φ_F = ~9%). The di-TPE substituted NDI (2,6-DTPEcNDI) in dilute solution has very low Φ_F = 0.09%, but its aggregates formed in $CHCl_3$/hexane mixture (f_h = 90%) and the powder sample emit efficient red to near infrared FL ($\lambda_{em,solid}$ = 717 nm, $\lambda_{em,aggr}$ = 681 nm, Φ_F = ~18%). Both the derivatives self-assembled into variety of microstructures in $CHCl_3$/ MeOH and $CHCl_3$/hexane and THF/water mixes *via* solvophobic control such as fibres, needle-like, nano-belts with controlled dimensions. The aromaticity of the NDI core along with the crystalline packing of terminal TPE moieties gives a unique design. The effect of the linking mode and number of substitutions on the NDI core on the AIE performance in an area of continuing research for us and will be reported on in due course. Nevertheless, these results will provide the way to the rational and controlled designs of nanostructures deriving AIE molecule and may allow construction of highly efficient luminescent solid materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of UV–vis fluorescence and microscopic data of aggregates in all the solvents. See DOI: 10.1039/c000000x/

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