Self-Assembled Donor-Acceptor Trefoils: Long-Lived Charge Separated State Through Aggregation

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Materials and methods: 4-bromo-1,8-naphthalic anhydride (95%), 2,6-diisopropylaniline (97%), 4-(diphenylamino)phenylboronic acid and tetrakis(triphenylphosphine)palladium(0) (99%) were purchased from Sigma Aldrich and used as such without further purification. Melting points (mp) were obtained using a capillary melting point apparatus and are reported without correction. IR spectra were recorded on a Shimadzu IR Prestige-21 FT-IR spectrometer as neat KBr pellets for all the derivatives. ¹H and ¹³C NMR spectra were measured on a 500 MHz and 125 MHz Bruker advanced DPX spectrometer respectively and 1,1,1,1tetramethylsilane (TMS) is used as the internal standard for ¹H and ¹³C NMR measurements. CHN analyses were carried out on an Elementar vario MICRO cube Elemental Analyzer. All values recorded in elemental analyses are given in percentages. High Resolution Mass Spectra (HRMS) were recorded on Agilent 6538 Ultra High Definition (UHD) Accurate-Mass Q-TOF-LC/MS system using either atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) mode. Photophysical measurements of the derivatives were carried out in a cuvette of 3 mm path length unless otherwise mentioned. Absorption and emission spectra were recorded on Shimadzu UV-3600 UV-VIS-NIR and Horiba Jobin Yvon Fluorolog spectrometers respectively. Solution state¹ relative quantum yield measurements were performed using $[Ru(bpy)_3]Cl_2$ hydrate in water as the reference (Reported quantum yield $\Phi_f = 0.045$) exciting at 450 nm. Lifetime measurements were carried out in an IBH picosecond time correlated single photon counting (TCSPC) system.^{2, 3} Pulse width of the excitation $(\lambda_{exc}=375 \text{ nm})$ source is determined to be <100 ps. The fluorescence decay profiles were de-convoluted using IBH data station software version 2.1, and fitted with exponential decay, minimizing the χ^2 values.

X-ray crystallography: Single yellow crystals of TNDI were grown by slow evaporation of dichloromethane: hexane (1:3). X-ray diffraction experiments were performed choosing high-quality crystals of approximately $0.20 \times 0.15 \times 0.10$ mm³ dimension. Crystallographic data collected are presented in the supporting information, Table S1. Single crystals were mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromatic MoK α radiation. The data were collected using Bruker APEXII detector and processed using APEX2 from Bruker. All structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined.

Dynamic light scattering (DLS): Dynamic light scattering (DLS) measurement of TN conjugates in THF (0.3 mM) was carried out on a Malvern Zeta Sizer Nano Zs equipped with 655 nm laser. The solutions of TNOH, TNDI, $T(NOH)_3$ and $T(NDI)_3$ for DLS analysis were prepared in THF and the experiment was carried out in a 3 mL square glass cuvette at 25 °C at a back scattering angle of 173°.

Transmission electron microscopy (TEM): TEM measurements were carried out on FEI Tecnai 30 G² high resolution transmission electron microscope and JEOL 2010 with an accelerating voltage of 100 kV. The samples were prepared by drop casting THF solution of 0.3 mM TN derivatives, on a 400 mesh carbon-coated copper grid (Ted Pella, Inc.) at ambient conditions and allowing the excess solvent to evaporate under air in dust free conditions. TEM images were obtained without staining. The average diameter of the particles was determined from the Lorentzian fit of the histogram of the particle size distribution curves.

Scanning electron microscopy (SEM): FE-SEM measurements of TN derivatives in THF was carried out on FEI Nova NanoSEM 450 (FEG type), drop casting 0.3 mM TN conjugates in THF on the flat surface of 400 mesh carbon-coated copper grid (Ted Pella, Inc.) and allowing to evaporate the excess solvent under air in dust free conditions. The sample was further subjected to thin chromium sputtering using JEOL JFC-1100 fine coater to increase the signal/noise ratio. The probing side was inserted into JEOL JSM-5600 LV scanning electron microscope for obtaining the images. The average diameter of the particles was determined from the Lorentzian fit of the size distribution curve.

Determination of fluorescence quantum yield and radiative and non-radiative rate constants:¹⁰ Solution state fluorescence quantum yields of TN derivatives were calculated by relative quantum yield method as follows,

$$\Phi_{\rm s} = \Phi_{\rm ref} \left(\frac{I_{\rm s}}{I_{\rm ref}}\right) \left(\frac{{\rm OD}_{\rm ref}}{{\rm OD}_{\rm s}}\right) \left(\frac{n_{\rm s}}{n_{\rm ref}}\right)^2 \tag{4}$$

wherein, Φ_s and Φ_{ref} are the quantum yields of sample and reference respectively, I_s and I_{ref} are the area under the emission spectrum for sample and reference respectively. OD_s and OD_{ref} are the absorbances of sample and reference respectively at the excitation wavelength. n_s and n_{ref} are the refractive index of the solvent in which sample and reference are taken.

Radiative (k_r) and non-radiative (k_{nr}) rate constants from the singlet excited states are calculated from the fluorescence quantum yields, Φ_f .

$$\Phi_{\rm f} = \frac{k_{\rm r}}{k_{\rm r} + k_{\rm nr}} \tag{5}$$

The rate constants k_r and k_{nr} can be evaluated by measuring fluorescence lifetimes (τ_f) from TCSPC measurements. The following equations depict relation between Φ_f , τ_f , k_r and k_{nr} .

$$k_r = \frac{\Phi_f}{\tau_f}$$
 and (6)

$$k_{\rm nr} = \frac{1 - \Phi_{\rm f}}{\tau_{\rm f}} \tag{7}$$

a change in Φ_f could be attributed to the changes in either k_r/k_{nr} . The enhancement in the quantum yield (Φ_f) with increased solvent polarity is due to the stabilization of the excited states by virtue of interaction with the solvent dipoles and decrease in the non-radiative (k_{nr}) rate constant.

Lippert-Mataga Analyses:¹⁰ Lippert-Mataga equation demonstrates the sensitivity of a molecule to the solvent polarity arising due to the changes in the excited state dipole moment relative to the ground state dipole moment. If the net change in dipole moment is zero (i.e. $\mu_e - \mu_g = 0$),¹¹ absorption and emission maxima of the chromophore should not change with solvent polarity. While, if the excited state dipole moment is larger than the ground state (i. e. $\mu_e > \mu_g$, positive slope for Lippert-Mataga plot), the absorption and emission maxima are anticipated to red shift with increased solvent polarity. The compounds which display such behavior possess charge transfer (CT) with ($\pi \rightarrow \pi^*$) excited states. Furthermore, if the dipole moment of the excited state decreases with respect to the ground state upon excitation ($\mu_e < \mu_g$, negative slope for Lippert-Mataga plot), the absorption and emission maxima are expected to show blue shift with increased solvent polarity. This occurs in molecules with ($n \rightarrow \pi^*$) excited states.

The degree of charge separation is estimated as follows, one Debye (1 D) unit is 1.0×10^{-18} esu cm. 4.8 D is the dipole moment that results from a charge separation of one unit charge (4.8 x 10^{-10} esu) by 1 Å (10^{-8} cm). Conversion of $\Delta\mu$ expressed in Debye into esu Å units is achieved dividing by a factor of 4.8 esu⁻¹Å⁻¹ which can provide the experimental charge separation in the molecule. Degree of charge separation (theoretical) in the molecule is obtained from centers of spin density distributions¹² (estimated as 2.13, 2.41, 2.31 and 1.97 esu⁻¹Å⁻¹ for TNOH, TNDI, TN(OH)₃ and TN(DI)₃ respectively using B3LYP/6-311G**+ level of theory).^{13-17,18}

Syntheses and characterization of TN conjugates:

Synthesis of NOH: 4-Bromo-1,8-naphthalic anhydride (0.50 g, 1.8 mmol, 1 eq.) was dissolved in 10 ml DMF and added 10 ml of dioxane. To this R(-)-2-amino-1-butanol (0.34 ml, 3.6 mmol, 2 eq.) was added. The reaction was refluxed with constant stirring for 24 hrs followed by bringing the reaction temperature to the room temperature. Product was precipitated from the reaction mixture by the addition of water (50 ml) followed by filtration and the product was thoroughly washed with methanol/water (1:1) solution. The crude product thus obtained was subjected to column chromatography (SiO₂, acetone:DCM, 1:9) to afford a white solid (69 %, m. p. = 173 °C). 1H NMR (500MHz, CDCl₃): δ =8.59 (m, 1H), 8.52 (m, 1H), 8.35 (d, J = 10 Hz, 1H), 7.98 (d, J = 5 Hz, 1H), 7.80 (m, 1H), 5.23 (m, 1H), 4.16 (m, 1H), 3.91 (m, 1H), 2.01 (m, 2H), 0.91 (t, J = 15 Hz, 3H); 13C NMR (125 MHz, CDCl₃): δ =164.82, 133.35, 132.37, 131.56, 131.17, 130.55, 129.10, 128.15, 123.13, 122.24, 77.27, 63.59, 57.32, 21.30, 11.00; IR (KBr): 3512.37, 3086.11, 2964.59, 2875.86, 1695.43, 1654.92, 1581.63, 1363.67, 1240.23, 1047.35, 975.98, 779.24. HR-MS (EI)-(m/z): 347.0542. Calcd for C₁₆H₁₄BrNO₃: 347.0521; Anal. Calcd for C₁₆H₁₄BrNO₃: C, 55.19; H, 4.05; N, 4.02. Found: C, 55.22; H, 3.99; N, 3.95.

Synthesis of NDI: To a solution of 1,8-naphthalic anhydride (5.05 mmol) in 100 ml of acetic acid, 2,6diisopropylaniline (50.5 mmol) was added and heated at 110 °C for 5 h. The reaction mixture was then cooled, filtered, washed with water and dried. Purification by column chromatography (silica gel, ethylacetate:hexane, 3:7) afforded NBr as a white solid (95%, m.p. 130 °C); ¹H NMR (500 MHz, CDCl₃): $\delta = 8.66$ (d, J = 10 Hz, 1H), 8.60 (d, J = 10 Hz, 1H), 8.42 (d, J = 10 Hz, 1H), 8.04 (d, J = 10 Hz, 1H), 7.84 (t, J = 15 Hz, 1H), 7.42 (t, J = 15 Hz, 1H), 7.26 (d, J = 10 Hz, 2H), 2.66 (m, 2H), 1.08 (d, J = 5 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃): $\delta =$ 133.61, 132.59, 131.75, 131.21, 130.94, 130.66, 130.56, 129.70, 129.63, 128.20, 124.07, 123.19, 122.31, 29.18, 23.96; IR (KBr): 2962.66, 2866.22, 1710.86, 1672.28, 1587.42, 1460.11, 1352.10, 1238.30, 1186.22, 962.48, 900.76, 783.10, 511.14 cm⁻¹; HR-MS (EI)-(m/z): 435.0389. Calcd. for C₂₄H₂₂BrNO₂: 435.0395; Anal. Calcd. for C₂₄H₂₂BrNO₂: C, 66.03; H, 5.11; N, 3.17. Found: C, 66.06; H, 5.08; N, 3.20.

Synthesis of TNOH: To a solution of 4-bromo-N-(-1-(hydroxymethyl)propyl)-naphthalene-1,8-dicarboximide (1.1 mmol) in 40 ml THF, 20 ml of 2 M aqueous K_2CO_3 solution was added under nitrogen atmosphere. To this solution, 1.1 mmol of 4-(diphenylamino)phenylboronic acid (TB) was added followed by Pd(PPh₃)₄ (14.7

μmol). The reaction mixture was heated at 70 °C for 12 h. The reaction mixture was allowed to cool down, and then it was extracted with dichloromethane. The solvent was removed under reduced pressure and the residue purified by column chromatography (silica gel, EtOAc:hexane, 5:5) to afford yellow amorphous TNOH powder (88%). m.p. 370 °C; ¹H NMR (500 MHz, CDCl₃): δ = 8.67 (d, J = 8.5 Hz, 2H), 8.45 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8 Hz, 2H), 7.87 (t, J = 10 Hz, 2H), 7.76 (t, J = 10 Hz, 2H), 7.40 (d, J = 10 Hz, 2H), 7.36 (d, J = 10 Hz, 2H), 7.24 (d, J = 8.5 Hz, 4H), 7.14 (d, J = 8.5 Hz, 2H), 5.35 (m, 1H), 4.26 (m, 1H), 4.03 (m, 1H), 2.12 (m, 2H), 1.03 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 148.44, 147.33, 146.98, 133.41, 133.02, 131.78, 131.21, 130.79, 129.92, 129.50, 128.99, 128.19, 127.76, 126.77, 125.08, 122.88, 122.47, 63.91, 57.03, 21.24, 11.02; IR (KBr): 3518.16, 3059.10, 2962.66, 1695.43, 1647.21, 1585.49, 1490.97, 1396.46, 1355.96, 1319.31, 1278.81, 1238.30, 1182.36, 1058.92, 783.10, 754.17, 696.30. HR-MS (EI)-(m/z): 513.2116. Calcd. for C₃₄H₂₈N₂O₃: 513.2108; Anal. Calcd. for C₃₄H₂₈N₂O₃: C, 79.67; H, 5.51; N, 5.46. Found: C, 79.65; H, 5.58; N, 5.49.

Synthesis of TNDI: To a solution of 4-bromo-N-(2,6-diisopropyl)-naphthalene-1,8-dicarboximide (1.1 mmol) in 30 ml THF, 15 ml of 2 M aqueous K_2CO_3 solution was added under nitrogen atmosphere. To this solution, 1.1 mmol of 4-(diphenylamino)phenylboronic acid (TB) was added followed by Pd(PPh₃)₄. The reaction mixture was heated at 70 °C for 12 h. The reaction mixture is then allowed to cool down, and further extracted with dichloromethane. The solvent was removed under reduced pressure and the residue is purified by column chromatography (silica gel, DCM:hexane, 4:6) to afford yellow amorphous TNDI in moderate yield (92%). ¹H NMR (500 MHz, CDCl₃): δ = 8.73 (d, J = 10 Hz, 2H), 8.52 (t, J = 10 Hz, 1H), 7.81 (t, J = 15 Hz, 2H), 7.51 (t, J = 15 Hz, 1H), 7.44 (d, J = 10 Hz, 2H), 7.38 (m, 6H), 7.28 (m, 6H), 7.15 (t, J = 15 Hz, 2H), 2.81 (m, 2H), 1.20 (m, 12H); ¹³C NMR (125 MHz, CDCl₃): δ = 164.40, 148.44, 147.34, 145.70, 133.14, 131.71, 131.45, 130.30, 129.52, 127.77, 126.77, 125.12, 124.02, 123.71, 122.48, 121.32, 29.16, 24.01. IR (KBr): 3030.17, 2960.73, 2866.22, 1703.14, 1664.57, 1585.49, 1489.05, 1357.89, 1278.81, 1236.37, 1188.15, 835.18, 754.17, 696.30. HR-MS (EI)-(m/z): 600.2771. Calcd. for C₄₂H₃₆N₂O₂: 600.2777; Anal. Calcd. for C₄₂H₃₆N₂O₂: C, 79.67; H, 5.01; N, 5.46. Found: C, 79.65; H, 5.08; N, 5.49.



Scheme S1: (i) Acetic acid; 110 °C; 5 h, (ii) Pd(PPh₃)₄; Anhyd. THF; 2 M K₂CO₃; 70 °C; 12 h.

Synthesis of T: Tris-(4-bromophenyl)-amine (0.54 g, 2.9 mmol, 1 eq) was dissolved in 4 ml of THF; followed by cooling it to -78 °C. n-BuLi (5.2 mmol, 1.79 eq, 3.25 ml) was added dropwise and kept at -78 °C for 1 hour. 2-isopropoxy-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane (26 mmol, 8.9 eq, 4.86 ml) was added drop wise. After addition, the reaction temperature was elevated to room temperature and stirring was continued overnight. 5 ml of H₂O was added to quench the reaction. The water layer was extracted with methylene chloride for 2-3 times and the combined organic layers were dried over Na₂SO₄. After the volatile solvent was removed under reduced pressure, it was subjected to purification by column chromatography (SiO₂, EtOAc:hexane,2:8) to yield

the product T as white crystals. (50 %, m. p. > 300 °C). ¹H NMR (500MHz, CDCl₃): δ = 7.61 (d, J = 8 Hz, 6H), 7.02 (d, J = 8 Hz, 6H), 1.233 (s, 36H), ¹³C NMR (125 MHz, CDCl₃): δ = 149.8, 135.9, 123.5, 83.7, 24.9. IR (KBr): 2980.02, 1597.06, 1359.82, 1321.24, 1284.59, 1143.79, 1091.71, 860.25, 657.73 cm⁻¹. HR-MS (EI)-(m/Z): 623.4502. Calcd for C₃₆H₄₈B₃NO₆: 623.4510; Anal. Calcd for C₃₆H₄₈B₃NO₆: C, 69.08; H, 7.76; N, 2.25. Found: C, 69.01; H, 7.70; N, 2.28.

Synthesis of T(NOH)₃: 4-bromo-N-(-1-(hydroxymethyl)propyl)-naphthalene-1,8-dicarboximide (93 mg, 0.256 mmol, 3.2 eq.) was dissolved in 30 ml anhydrous THF and stirred in a N₂ atmosphere for 5 minutes. To this 15 ml of 2 M aqueous K₂CO₃ was added and stirred. T (50 mg, 0.08 mmol, 1 eq.) was added and stirred in N₂ atmosphere again for 5 minutes. Pd[(PPh₃)₄] (0.89 mg, 0.01 mmol) was added and the temperatures was increased to 70 °C, and refluxed for 12 hrs. THF was removed by rotary evaporation and compound was extracted using DCM. The DCM layer was dried and the crude product obtained was subjected to column chromatography (SiO₂, acetone:DCM,1:9) to afford an orange fluorescent solid (90 %, m. p. > 300 °C). ¹H NMR (500MHz, CDCl₃): δ = 8.61 (m, 6H), 8.38 (d, J = 8.25 Hz, 3H), 7.72 (d, J = 9.5 Hz, 6H), 7.48 (d, J = 8.3 Hz, 6H), 7.42(d, J = 8.3 Hz, 6H), 5.27 (d, J = 6 Hz, 3H), 4.19 (t, J = 12 Hz, 3H), 3.94 (t, J = 12 Hz, 3H), 2.06 (m, 6H), 1.98 (s, 3H), 0.98 (t, J = 9 Hz, 9H). ¹³C NMR (125 MHz, CDCl₃): δ = 165.4, 147.5, 146.9, 133.8, 132.7, 131.6, 131.3, 129.8, 128.9, 127.9, 126.9, 124.4, 123.0, 121.6, 63.8, 57.1, 21.3, 11.0. IR: 3462.22, 2926.01, 2873.94, 1697.36, 1651.07, 1583.56, 1504.48, 1462.04, 1396.46, 1354.03, 1319.31, 1238.30, 1184.29, 1056.99, 837.11, 785.03, 759.95 cm⁻¹.HR-MS (EI)-(m/z): 1047.1661: Calcd. for C₆₆H₅₄N₄O₉: C, 75.70; H, 5.20; N, 5.35. Found: C, 75.66; H, 5.18; N, 5.39.



Scheme S2: (i) Acetic acid; 110 °C; 5 h, (ii) Pd[(PPh₃)₄]; Anhyd. THF; 2 M K₂CO₃; 70 °C; 12 h.

Synthesis of T(NDI)₃: The 4-bromo-N-(2,6-diisopropyl)-naphthalene-1,8-dicarboximide (104.4 mg, 0.256 mmol, 3.2 eq.) was dissolved in 30 ml anhydrous THF and stirred in a N₂ atmosphere for 5 minutes. To this 15 ml of 2 M aqueous K₂CO₃ was added and stirred. T (50 mg, 0.08 mmol, 1 eq.) was added and stirred in N₂ atmosphere again for 5 minutes. Pd[(PPh₃)₄] (0.89 mg, 0.01 mmol) was added and the temperatures was increased to 70 °C, and refluxed for 12 hrs. THF was removed by rotary evaporation and compound was extracted using DCM. The DCM layer was dried and the crude product obtained was subjected to column chromatography (SiO₂, DCM: hexane, 6:4) to afford an orange fluorescent solid (82 %, m. p. > 300 °C). ¹H NMR (500 MHz, CDCl₃): $\delta = 8.68$ (q, J = 13 Hz, 6H), 8.46 (d, J = 8 Hz, 2H), 7.77 (d, J = 8.5 Hz, 4H), 7.72 (d, J

= 7 Hz, 2H), 7.53 (d, J = 8.5 Hz, 4H), 7.48 (m, 5H), 7.44 (m, 5H), 7.33 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 6H), 2.71 (m, 6H), 1.42 (s, 36H). ¹³C NMR (125 MHz, CDCl₃): δ = 163.28, 147.5, 146.9, 132.93, 131.81, 130.79, 130.40, 130.24, 130.12, 129.80, 129.24, 128.48, 126.89, 125.93, 123.47, 123.03, 122.82, 122.08, 120.70, 29.17, 22.97. IR: 2923.25, 2861.53, 1708.09, 1667.59, 1586.58, 1503.64, 1463.13, 1358.98, 1316.54, 1237.46, 1187.31, 836.27, 784.19 cm⁻¹. HR-MS (EI)-(m/z): 1311.6122: Calcd. for C₉₀H₇₈N₄O₆: 1311.6125; Anal. Calcd. for C₉₀H₇₈N₄O₆: C, 82.41; H, 5.99; N, 4.27. Found: C, 82.38; H, 5.95; N, 4.24.

Table S1:	Crystal	data and	structure refinement	of TNDI.
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Unit cell parameters	TNDI
Empirical formula	$C_{42}H_{36}N_2O_2$
Formula weight	600.73
a (Å) :	23.1475(13)
b (Å) :	23.1475(13)
c (Å) :	12.6145(9) A
α(alpha):	90°
β(beta):	90°
γ(gamma):	90°
Volume $(Å^3)$:	6758.9(7)
Crystal system	Tetragonal
Space group:	$P4_2/n$
Calculated density (mg/m ³):	1.181
Z:	8
Temperature (K) :	296(2)
R (F, %):	9.58
$R_{w}(F^{2})$:	1.066
CCDC Number	1490062

Table S2: Particle size distribution of TNOH, TNDI, $T(NOH)_3$ and $T(NDI)_3$ in THF obtained from DLS, SEM, TEM, AFM and confocal measurements.

	DLS	SEM	TEM	AFM	Confocal
	(Size,	(Size,	(Size,	(Size,	(Size,
	± 100 nm)	± 50 nm)	± 40 nm)	± 60 nm)	± 80 nm)
TNOH	727, 5500	236	437	370	279
TNDI	1220	526	672, 1150	845, 1150	660
T(NOH) ₃	467	272	500	271	260
T(NDI) ₃	700	451	322	773	476

Table S3: Geometry optimized $(B3LYP/6-311G^{**}+ \text{ level of theory})$ calculations and redox properties of representative TN conjugates [TNDI and T(NDI)₃].

		Energy (e	eV)		$E_{g}(eV)$	Redox Po	tential (V)
	HOMO-1	HOMO	LUMO	LUMO+1	$(E_{LUMO}-E_{HOMO})$	E _{ox}	E _{red}
TNDI	-6.45	-5.57	-2.71	-1.36	2.86	1.17	-1.22
T(NDI) ₃	-6.32	-5.68	-2.73	-2.73	2.94	0.94	-1.17

Table S4: Solvent polarity dependent photophysical measurements of TNOH, TNDI, TN(OH)3 and TN(DI)3.

Solvent	TNOH			TNDI			T(NOH)	3		T(NDI) ₃		
	λ^{a} (nm)	λ^{b} (nm)	τ^{c} (ns)	λ^{a} (nm)	λ^{b} (nm)	τ^{c} (ns)	λ^{a} (nm)	λ^{b} (nm)	τ^{c} (ns)	λ^{a} (nm)	λ^{b} (nm)	τ^{c} (ns)
Hexane	415	477	3.92	413	467	4.05	414	500	4.65	405	456	2.55
Toluene	412	534	5.36	424	511	4.96	426	529	4.85	415	516	3.65

DCM	417	656	2.63	421	591	5.39	415	590	5.52	427	562	6.99
CHCl ₃	421	611	5.65	431	606	7.43	427	635	6.67	430	585	6.27
THF	417	624	0.68	433	620	1.25	408	618	1.86	427	613	6.47
ACN	423	711	2.56	434	636	3.74	425	635	2.51	428	600	0.38
			(17%),			(12%),			(5%),			(87%),
			0.17			0.14			0.36			0.62
			(83%)			(88%)			(95%)			(13%)
MeOH	421	672	1.26	431	675	2.99	431	638	1.69	428	690	$\leq 0.1^{\acute{d}}$
			(37%),			(99%),			(59%),			
			0.29			0.19			0.32			
			(63%)			(1%)			(41%)			
DMSO	428	722	2.41	435	700	2.64	431	696	0.43	434	711	0.14
			(8%).			(41%).						(10%).
			0.22			9.30						0.39
			(92%)			(44%).						(90%)
			(=)			0.19						(,,,,,)
						(15%)						

^a-absorption; ^b-emission; ^c-time-resolved fluorescence measurements performed exciting the samples at 440 nm; ^d-within the pulse width of the instrument.

Table S5: Variation of fluorescence quantum yield (QY) of TN derivatives with solvent polarity.

Sample	Solution	n state QY	Reduction in	
	DCM	THF	$\Phi_{_{ m f}}$	
TNOH	22	26	0.37	70
TNDI	30	35	0.42	83
T(NOH) ₃	25	33	0.75	44
T(NDI) ₃	35	54	0.88	61

Table S6: Lifetimes of TN derivatives obtained from kinetic analyses of nTA spectra (λ_{exc} = 355 nm).

		TNOH		TNDI		T(NOH) ₃		T(NDI) ₃	
		N_2 purging $(\tau, \pm 0.1 \text{ us})$	O_2 purging $(\tau, \pm 0.01 \text{ ns})$	N_2 purging $(\tau, \pm 0.1 \text{ us})$	O_2 purging (τ , ± 0.01 ns)	N_2 purging $(\tau, \pm 0.1 \text{ µs})$	O_2 purging (τ , ± 0.01 ns)	N_2 purging $(\tau, \pm 0.1 \text{ us})$	O_2 purging (τ , ± 0.01 ns)
nTA	ACN	0.87	96.83	0.57	29.21	1.87	9.20	1.54	16.32
	THF	0.38	35.62	2.89	10.83	3.42	2.38	5.36	40.54

Table S7: Lifetimes of TN derivatives obtained from kinetic analyses of fTA spectra (λ_{exc} = 400 nm).

	ACN (t, :	± 0.035 ps)	THF (t, ± 0.053 ns)				
	V_1^{a}	$V_2^{\hat{a}}$	V_1^{a}	V_2^{a}	V_3^a		
TNOH	121.98	10.28	3.08	0.93	1.31		
TNDI	136.76	175.61	7.37	0.50	0.24		
T(NOH) ₃	421.39	223.45	3.44	2.62	0.78		
$T(NDI)_3$	315.22	263.41	2.21	1.37	4.31		
^a - monoex	ponential l	kinetic coi	nponents	were fit	ted with		
first order rate equation of the form $y = A^* exp(-$							
x/τ)+consta	ant.						

Sl No	Contributed by	C ₃ -symmetrical architecture	Reference	Purpose
1	Our data	Triphenylamine-naphthalimide dyads and trefoils		Comparison of photoinduced electron transfer in the aggregated state.
2	S. J. George, T. K. Maji and coworkers	triphenylamine(T)-perylenediimide(PDI)	Chem. Mater. 2012, 24, 969-971.	Porous material for N ₂ adsorption.
3	F. Wudl and coworkers	decacyclene triimides (DTI)	 (i). Angew. Chem. Int. Ed. 2013, <i>52</i>, 1446-1451. (ii). Angew. Chem. Int. Ed. 2015, <i>54</i>, 6775-6779. 	Photoinduced electron transfer in the monomeric state.
4	M. R. Wasielewski and coworkers	1,3,5-triphenylbenzene(P)- perylenemonoimide(PMI)	J. Phys. Chem. Lett. 2014, 5, 1608-1615.	Excitation energy transfer in the aggregated state.
5	M. R. Wasielewski and coworkers	P-PDI	J. Am. Chem. Soc. 2006, 128, 1782-1783.	Photoinduced electron transfer in the aggregated state in presence of TEA.
6	C. F. J. Faul and coworkers	Melamine(M)-PDI	Macromolecules 2015 , <i>48</i> , 2064-2073.	Microporous material for CO ₂ adsorption.
7	S. Yamaguchi and coworkers	triphenylborane mesogens	Angew. Chem. Int. Ed. 2015, 54, 6922-6925.	Charge carrier transport.
8	M. R. Wasielewski and coworkers	tetrahedral tetraphenylmethane-PDI	J. Phys. Chem. C. 2014 , <i>118</i> , 16941-16950.	Excitation energy transfer in the aggregated state.
9	M. R. Wasielewski and coworkers	ethynyl-P-linked chlorophylls	 (i). Angew. Chem. Int. Ed. 2006, 45, 7979-7982. (ii). Chem. Commun. 2010, 46, 401-403. 	Excitation energy transfer in the aggregated state.
10	Z. Wang and coworkers	tetraphenyladamentyl- naphthalenediimide(NDI)	J. Phys. Chem. C. 2014, 118, 17585-17593.	CO_2 capture.

Table S8: A comparative account of the C_3 -symmetrical donor-acceptor molecular architectures reported in various literatures.



Figure S1: (a) π - π , (b) C-H•••O and (c) C-H•••H-C interactions observed in crystalline TNDI.



Figure S2: (a), (b) two dimensional crystal structure arrangement in TNDI.



Figure S3: (a) Hirshfeld structure analyses of TNDI representing (d), (e), (f), (g) π - π , C•••H, H•••H and O•••H interactions. (b) d_{norm} and (c) electrostatic surface potential maps of TNDI.



Figure S4: (a) Particle size distribution for TN conjugates obtained from DLS. (b) AFM image of $T(NOH)_3$ (first row) and $T(NDI)_3$ (second row) as drop-casted from THF.



Figure S5: Morphological analyses of TNOH (first row) and TNDI (second row) as drop-casted from THF. Selected area electron diffraction (SAED) patterns of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ respectively.



Figure S6: Particle size distribution of TNOH, TNDI, T(NOH)₃ and T(NDI)₃ obtained from (a) DLS, (b) SEM, (c) TEM, (d) AFM and (e) confocal measurements.



Figure S7: Schematic representation of formation of spherical/vesicular aggregates of TN conjugates in THF.



Figure S8: Representative frontier molecular orbital analyses of TNDI and $T(NDI)_3$ performed at B3LYP/6-311G+** level of theory.



Figure S9: (a) absorption and (b) emission spectrum of T and N in ACN. (c) absorption, (d) emission, (e) excitation spectra and (f) time-resolved fluorescence decay profiles ($\lambda_{exc} = 440$ nm) of TN conjugates in ACN.



Figure S10: Solvent-polarity dependent (a-b) absorption and (c-d) emission measurements of TNOH and TNDI.



Figure S11: Solvent-polarity dependent (a-b) absorption and (c-d) emission measurements of $T(NOH)_3$ and $T(NDI)_3$.



Figure S12: Solvent-polarity dependent time-resolved fluorescence decay profiles of (a) TNOH, (b) TNDI, (c) T(NOH)₃ and (d) T(NDI)₃ ($\lambda_{exc} = 440$ nm).



Figure S13: Solvent-polarity dependent Lippert-Mataga plots of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$.



Figure S14: Concentration dependent (a-b) absorption and (c-d) emission measurements of TNOH and TNDI in THF.



Figure S15: Concentration dependent (a-b) absorption and (c-d) emission measurements of $T(NOH)_3$ and $T(NDI)_3$ in THF.



Figure S16: Concentration dependent excitation spectral measurements of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ respectively in THF.



Figure S17: Concentration dependent (a-b) absorption and (c-d) emission measurements of TNOH and TNDI in ACN.



Figure S18: Concentration dependent (a-b) absorption and (c-d) emission measurements of $T(NOH)_3$ and $T(NDI)_3$ in ACN.



Figure S19: Concentration dependent excitation spectral measurements of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ respectively in ACN.



Figure S20: nTA measurements of (a) TNOH, (b) TNDI, (c) T(NOH)₃ and (d) T(NDI)₃ respectively in ACN.



Figure S21: DAS obtained for nTA measurements of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ respectively in ACN from SVD followed by global analysis excited at 355 nm.



Figure S22: Kinetic profiles of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ in ACN monitored at 550 nm, obtained from nTA measurements.



Figure S23: nTA measurements of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ respectively in THF.



Figure S24: DAS obtained for nTA measurements of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ respectively in THF from SVD followed by global analysis excited at 355 nm.



Figure S25: Kinetic profiles of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ in ACN monitored at 550 nm, obtained from nTA measurements.



Figure S26: UV-Vis absorption spectra of chemically (a) oxidized T and (b) reduced N. UV-Vis absorption spectra of electrochemically (c) oxidized T (potential = 1.5 V) and (d) reduced N (potential = -1.6 V). The chemical oxidation of T unit was carried out by successive addition of 10 µL volumes of 1 mM Cu(II) triflate to a 1 µM solution of T in ACN. For chemical reduction of naphthalimide 10 µL volumes of 1 mM tetra-n-butylammonium fluoride to a 1 µM solution of N in ACN is used and all the measurements were performed in ACN).



Figure S27: fTA measurements of (a) TNOH, (b) TNDI, (c) T(NOH)₃ and (d) T(NDI)₃ respectively in ACN.



Figure S28: Right singular vectors obtained for (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ respectively obtained after global analysis of fTA spectra in ACN.



Figure S29: Left singular vectors obtained for (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ respectively obtained after global analysis of fTA spectra in ACN.



Figure S30: fTA measurements of (a) TNOH, (b) TNDI, (c) T(NOH)₃ and (d) T(NDI)₃ respectively in THF.



Figure S31: Right singular vectors obtained for (a) TNOH, (b) TNDI, (c) T(NOH)₃ and (d) T(NDI)₃ respectively obtained after global analysis of fTA spectra in THF.



Figure S32: Left singular vectors obtained for (a) TNOH, (b) TNDI, (c) T(NOH)₃ and (d) T(NDI)₃ respectively obtained after global analysis of fTA spectra in THF.



Figure S33: (a) cyclic voltammetric measurements of TN conjugates in ACN.



Figure S34: Steady-state UV-Vis absorption spectra of (a) TNOH, (b) TNDI, (c) $T(NOH)_3$ and (d) $T(NDI)_3$ in THF recorded before and after laser irradiation.

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