Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Chiral induction by helical neighbour: Spectroscopic visualization of macroscopic-interaction among self-sorted donor and acceptor π-stacks

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Materials and Methods

All reagents were purchased from Sigma Aldrich Chemical Co. and used without further purification. Solvents were received from commercial sources and purified by prescribed methods.[1] For UV/vis experiments, spectroscopic grade solvents were purchased from Spectrochem. ^{1}H NMR spectra were recorded on a Bruker DPX-300 MHz and 500 MHz NMR spectrometer and all the spectra were calibrated against TMS. The elemental compositions of the purified compounds were confirmed by elemental analysis (Perkin-Elmer Series-II, CHNO/S Analyzer-2400). UV-Visible spectra were recorded in a Perkin-Elmer Lambda 25 spectrometer equipped with a peltier system for variable temperature experiments. Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a Q-tof-micro quadruple mass spectrometer (Micro mass). Atomic force microscopy (AFM) images were obtained by an AUTOPROBE CP base unit, di CP-II instrument, model no.AP-0100. Circular Dichroism (CD) experiments were carried out in a JASCO CD spectrometer (model-J815) equipped with a peltier for temperature variation experiments.

UV-visible spectroscopic studies: Stock solutions of different chromophores were made in $CHCl_3$ (2.0 mM). An aliquot (0.1 ml) was taken and was added with an appropriate amount of methylcyclohexane (MCH) to adjust the desired solvent composition and final concentration (0.1 mM). For self-sorting experiments, 0.05 ml stock solutions of individual components (DAN and NDI) in $CHCl_3$ were mixed together and then appropriate amount of MCH was added to the mixture to adjust the desired solvent composition. The solutions were allowed to equilibrate at rt for 2 h before spectral

measurements. For methanol experiments a solution of a particular chromophore in MCH/ $CHCl_3$ (95:5) was taken and methanol was added and spectra were recorded. For variable-temperature experiments a particular chromophore solution in MCH/ $CHCl_3$ (95:5) was heated from lowest to highest temperature and allowed to equilibrate for 15 min at the desired temperature before each measurement.

Mole fraction of aggregate (α_{agg}) at each solvent composition was estimated using equation 1.

$$\alpha_{agg} \approx \frac{A_{mix} - A_{mon}}{A_{agg} - A_{mon}} \qquad (1)$$

The absorbance at 382 nm for the NDI chromophore in $CHCl_3$ and MCH/ $CHCl_3$ (95:5) were taken as the A_{mon} and A_{agg}, respectively. A_{mix} is the absorbance at 382 nm at a given solvent mixture. The α_{agg} values at various solvent mixtures for **NDI-1** are plotted as a function of the solvent composition in the main text in **Fig** 1b. From the plot the critical solvent composition (MCH/ $CHCl_3$ (v/v) ratio) in which the mole fraction of the aggregate is 0.5 (α_{50}) was estimated and reported**.**

Similarly in variable-temperature experiment the α_{agg} at each temperature was determined by Equation 2

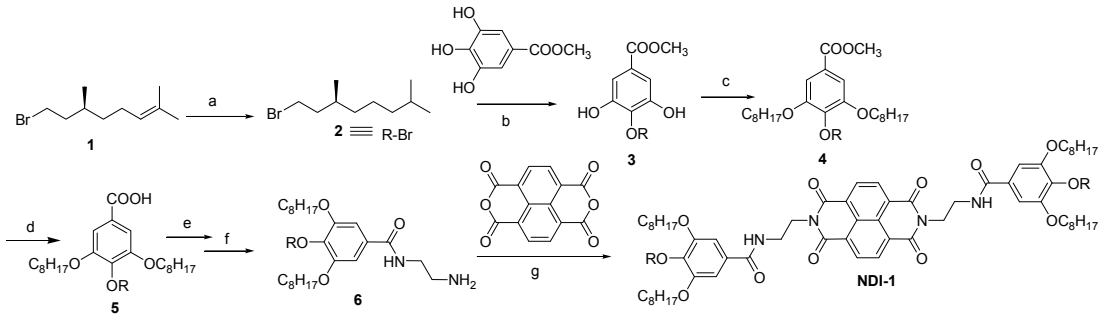
$$\alpha_{agg\,(T)} \approx \frac{A(T) - A_{mon}}{A_{agg} - A_{mon}} \qquad (2)$$

The absorbance at 382 nm for the NDI chromophore in $CHCl_3$ and MCH/ $CHCl_3$ (95:5) were taken as the A_{mon} and A_{agg}, respectively. A_T is the absorbance at 382 nm in between monomeric and aggregated state at a particular temperature. The α_{agg} (T) values at various temperatures for **NDI-1** are plotted as a function of the temperature in Fig S1b. From the plot, α_{50}(T) (the temperature in which the mole fraction of the aggregate is 0.5) was estimated and reported**.**

Atomic Force Microscopic (AFM) Studies: In a typical AFM experiment, 20 µl solution (95 % MCH in $CHCl_3$, concentration = 0.05 mM) of the chromophore was placed on a microscopic cover glass and then allowed to air dry overnight before the images were taken.

Circular Dichroism (CD) studies: In a typical experiment, stock solution of NDI and DAN chromophores was made in $CHCl_3$ (20 mM). An aliquot (0.05ml) was taken and was added with an appropriate amount of methylcyclohexane (MCH) to adjust the desired solvent composition and final concentration (0.5 mM). For self-sorting experiments, 0.05 ml stock solutions of individual components (DAN and NDI) in $CHCl_3$ were mixed together and then appropriate amount of MCH was added to the mixture to adjust the desired solvent composition. In each experiment individual chromophore concentration was kept fixed at 0.5 mM. All the experiments were carried out in a 1mm cuvette. The scan range was 200-500 nm at the rate of 500 nm /min.

Synthesis: Synthesis of **NDI-2** and **DAN-1** were described in our previous publications.[2] Synthetic route for other two chromophores (**NDI-1** and **DAN-2**) are described here.



Reagents and conditions: a) PtO_2, Ethyl acetate, H_2 (30 psi), 19 h, 93 %, b) K_2CO_3, DMF, 80 °C, 24 h, 44 % c) n-octyl bromide, K_2CO_3, DMF, 80 °C, 24 h, 76 % d) KOH, EtOH/H_2O, 100 °C, 6 h, 77 % e) $SOCl_2$, CH_2Cl_2, rt, 12 h f)ethylene diamine, CH_2Cl_2, 0 °C- rt, 6 h, 90 % g) DMF, 140 °C, 12 h, 57%

Scheme S1: Synthesis of **NDI-1**

Compound 2: A solution of compound **1** (2.6 g, 11.86 mmol) in ethyl acetate (30 mL) was placed in a high pressure hydrogenation vessel and the chamber was evacuated and was added with 47.0 mg PtO_2 and then the reaction mixture was subjected to mechanical shaking at 30 psi H_2 pressure for 19 h. Then the shaking was stopped, the reaction mixture was filtered and washed several times with ethyl acetate and finally the solvent was evaporated to get the crude product as light yellow oil (93 %). As the compound was found to be adequately pure from TLC and ^{1}H NMR, it was taken to the next step as such without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ (ppm) = 3.49-3.35 (2H, m), 1.91-1.86 (1H, m), 1.67-1.50 (3H, m), 1.17-0.89 (6H, m), 0.89-0.85 (m, 9H); HRMS (ESI): m/z calcd for $C_{10}H_{22}Br$ $[M+H]^+$: 221.0907; found: 221.0905.

4-[(S)-3,7-Dimethyloctyloxy]-3,5-dihydroxymethyl benzoate (3)[3]: Commercially available tri-hydroxymethylbenzoate (2.0 g, 10.8 mmol), (S)-3,7-dimethyloctyl bromide (2.36 g, 10.6 mmol), anhydrous K_2CO_3 (1.5 g, 10.8 mmol), and 25 mL DMF were mixed in a round bottom flask and the mixture was stirred at 80 °C for 24 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and poured in 250 mL of ice-cold water and then extracted with diethyl ether (3 × 50 mL). The combined organic layer was washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated to get the crude product as light brown color oil. It was purified by column chromatography using silica gel as stationary phase and 3% ethyl acetate in $CHCl_3$ as eluent to obtain pure product as colorless oil (44%). ^{1}H NMR ($CDCl_3$, 300 MHz, , TMS): δ (ppm) = 7.19 (s, 2H), 4.13-4.04 (m, 2H), 3.83 (s, 3H), 1.77-1.74 (m, 1H), 1.53-1.42 (m, 3H), 1.26-1.06 (m, 6H), 0.86 (d, 3H, J = 6.3 Hz) and 0.79 (d, 6H, J = 6.6 Hz); UV-visible (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 306 (1,451), 295 (2,194), 260 nm (8,386 $M^{-1}cm^{-1}$); HRMS (ESI): m/z calcd for $C_{18}H_{29}O_5$ $[M+H]^+$: 325.2024; found: 325.2031.

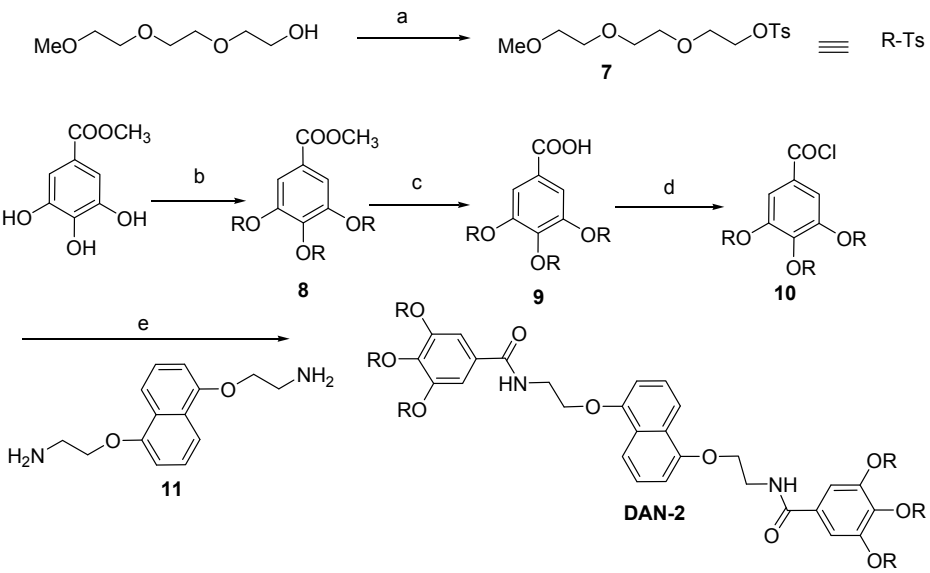
3-Octyloxy-4-[(S)-3,7-dimethyloctyloxy]5-hydroxymethyl benzoate (4)[3]: Compound **3** (1.322 g, 4.075 mmol), anhydrous K_2CO_3 (2g, 14.26 mmol), n-octyl bromide (1.652 g, 8.557 mmol) and 20 mL DMF were taken together in a round bottom flask and was stirred at 80 °C for 24 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and poured in 250 mL of ice-cold water and then extracted with diethyl ether (3 × 50 mL). The combined organic layer was washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated to get the crude product as light brown color oil. It was purified by column chromatography using basic alumina as stationary phase and 50% pet-ether in CH_2Cl_2 as eluent to obtain pure product as colorless oil (76%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ (ppm) = 7.24 (s, 2H), 4.02-3.98 (m, 6H), 3.87 (s, 3H), 1.81-1.79 (m, 5H), 1.57-1.44 (m, 7H), 1.35-1.27 (m, 18H), 1.13-1.11 (m, 4H), 0.87-0.84 (m, 15H); UV-visible (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 305 (2,297), 269 (8,772 $M^{-1}cm^{-1}$). HRMS (ESI): m/z calcd for $C_{34}H_{61}O_5$ $[M+H]^+$: 549.4521; found: 549.4521.**Synthesis of Compound 5, 6 and NDI-1**: Exactly identical procedure was followed as described in our previous publication.[2]

Compound 5: ^{1}H NMR ($CDCl_3$, 300 MHz, , TMS): δ (ppm) = 7.31 (s, 2H), 4.09-3.99 (m, 6H), 1.99-1.77 (m, 8H), 1.54-1.47 (m, 4H), 1.31-1.28 (m, 22H), 0.93-0.85 (m, 15H); UV-visible (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 305 (2,819), 268 (10,000 $M^{-1}cm^{-1}$). HRMS (ESI): m/z calcd for $C_{33}H_{53}O_5Na$ $[M+Na]^+$: 557.4182; found: 557.4182.

Compound 6: ^{1}H NMR (500 MHz, , TMS): δ (ppm) = 7.16 (s, 2H), 4.02-3.95 (m, 6H), 3.73-3.67 (m, 4H), 1.83-1.70 (m, 8H), 1.52-1.44 (m, 4H)1.30-1.14 (m, 22H), 0.92-0.85 (m, 15H); UV-visible (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 304 (1,352), 261 (11,864), 229 (19,196 $M^{-1}cm^{-1}$). HRMS (ESI): m/z calcd for $C_{35}H_{65}N_2O_4$ $[M+H]^+$: 577.4946; found: 577.4938.

Compound NDI-1: m.p. 175°C ; ^{1}H NMR ($CDCl_3$, 300 MHz, $CDCl_3$,TMS): δ (ppm) = 8.75 (s,4H), 6.90 (s, 4H), 4.53 (t, 4H, J = 4Hz), 3.95-3.89 (m, 12H), 3.84 (t, 4H, J = 4Hz), 1.83-1.76 (m, 10H), 1.58-1.42 (m, 14H), 1.31-1.25 (m, 44H), 1.17-1.13 (m, 6H) 0.92-0.85 (m, 24H); ^{13}C NMR ($CDCl_3$,): δ (ppm) = 160.76, 153.29, 142.32, 131.72, 126.82, 125.63, 106.35, 77.27, 77.01, 76.76, 73.59, 69.36, 31.91, 31.84, 30.36, 29.55, 29.38, 29.36, 29.30, 26.09, 22.7, 22.67, 14.09; UV-visible ($CHCl_3$): λ_{max} (ε) = 382 nm (23,203), 361 nm (19,364), 344 nm (11,479 $M^{-1}cm^{-1}$); HRMS (ESI): calcd for $[M + H]^+$: 1385.9619; found: 1385.9621; Elemental analysis: cald. for $C_{84}H_{128}N_4O_{12}$, C- 72.80, H- 9.31, N- 4.04, found C- 72.76, H- 9.35, N- 4.05.

Synthesis of DAN-2: Synthetic procedure is outlined in Scheme S2.



Reagents and conditions: a) TsCl, THF/ H_2O, NaOH, 5 h, 0o C- rt, 95 %; b) R-Ts, K_2CO_3, KBr, CH_3CN, 80 °C, 18 h, 95 % c) KOH, MeOH, THF, 12 h, 66% d) $SOCl_2$, CH_2Cl_2, rt, e) CH_2Cl_2, Et_3N, 12 h, 0 °C- rt, 79 %

Scheme S2: Synthesis of **DAN-2**

Compound 7: To a solution of tri-ethyleneglycol monomethyl ether (3.0 g, 0.0182 mmol) in THF (40 mL), 5mL aqueous NaOH solution (0.025 mmol) was added and the reaction mixture was cooled to 0 ^{o}C. To this cold solution, a solution of TsCl (3.82g, 0.020mmol) in THF (5mL) was added drop-wise and after the addition was over the reaction mixture was at rt for additional 5 h. The stirring was stopped and the contents were poured in 150 ml ice-cold water and extracted with $CHCl_3$ (3 × 50 mL). The combined organic extract was washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated to get the crude product which was purified by column chromatography using silica gel as stationary phase and petroleum ether/ethyl acetate mixture as eluent to get pure product as colorless oil (95 %). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 7.72 (2H, d, J =8.1 Hz), 7.27 (2H, d, J = 8.1 Hz), 4.09 (2H, t, J = 4.8 Hz), 3.61 (2H, t, J = 4.8 Hz), 3.55-3.52 (6H, m), 3.47-3.44 (2H, m), 3.30 (3H, S), 2.38 (3H, S); HRMS (ESI): m/z calcd for $C_{14}H_{23}O_6S$ $[M+H]^+$: 319.1217; found: 319.1211.

Compound 8: Trihydroxy-methylbenzoate (1.0 g, 5.4 mmol), compound **7** (5.18 g, 16.2 mmol),anhydrous K_2CO_3 (3.75 g, 27.2 mmol), and catalytic amount of KBr were mixed in a round bottom flask along with 20 mL DMF and the reaction mixture was stirred at 80 °C for 48 h under N_2 atmosphere. The heating was stopped and the reaction mixture was cooled to room temperature and CH_3CN was evaporated under reduced pressure. 250 mL of ice-cold water was added to pasty mass and the desired compound was extracted for the mixture with dichloromethane (3 × 50 mL). The combined organic extract was washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated to get the crude product as light-brown oil (95%). As the compound was found to be adequately pure from TLC and ^{1}H NMR, it was taken to the next step as such without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 7.26 (s, 2H), 4.19-4.15 (m, 6H), 3.85-3.82 (m, 7H), 3.76 (m, 2H), 3.70-3.68 (m, 6H), 3.66-3.58 (m, 12H), 3.58-3.51 (m, 6H) and 3.24 (s, 9H); UV-visible (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 295 (4,914), 265nm (11,675 $M^{-1}cm^{-1}$). HRMS (ESI): m/z calcd for $C_{29}H_{50}O_{14}Na$ $[M+Na]^+$: 645.3099; found: 645.3098.

Compound 9: Compound **8** (1g, 1.6 mmol), 1M aqueous KOH (10 ml), THF (10 ml), MeOH (10 ml) and KOH pellets (1g, 17.8 mmol) were taken in a round bottomed flask and the reaction mixture was refluxed at 100 ^{o}C for 12 h. The heating was stopped and the solvent was evaporated under reduced pressure to get a pasty mass to which 30 ml cold H_2O and 5 ml of concentrated HCl were added and stirred at rt for 20 min. To the clear solution, NaCl powder was added for salting out the product which was then extracted with ethyl acetate (3 x 30 ml). The combined organic extract was dried over anhydrous Na_2SO_4 and the solvent was evaporated to get the crude product as light brown color oil (66 %) which was characterized by TLC and ^{1}H NMR. As the crude product was found to be adequately pure, it was taken to the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 7.34 (s, 2H), 4.25-4.13 (m, 6H), 3.86-3.88 (m, 4H), 3.80-3.79 (m, 2H), 3.74-3.71 (m, 6H), 3.68-3.62 (m, 12H), 3.56-3.54 (m, 6H) and 3.24(s, 9H); UV-visible (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 295 (4,705), 265nm (11,200 $M^{-1}cm^{-1}$). HRMS (ESI): m/z calcd for $C_{28}H_{48}O_{14}Na$ $[M+Na]^+$: 631.2942; found: 631.2943.

Compound DAN-2: [4]A solution of compound **10** (0.65 g, 1.069 mmol) in 5 ml dry dichloromethane was added drop wise to an ice-cold solution of compound **11**[4] (0.125 g, 0.590 mmol) and triethylamine (0.18 ml) in 10 mL dry dichloromethane under N_2 atm. After the addition was over the reaction mixture was stirred in the ice-bath for another 2 h followed by rt stirring for additional 12 h. Then it was extracted with dichloromethane and washed with H_2O (3 x 30 mL) and brine (1 x 30 mL) and the organic extract was dried over anhydrous Na_2SO_4 and the solvent was evaporated to get the crude product. It was purified by column chromatography with silica gel as the stationary phase and 2% MeOH in dichloromethane as the eluent to get the pure product as light yellow oil (79 %). ^{1}H NMR (300 MHz, $CDCl_3$,TMS): δ(ppm) = 7.85 (d,2H), 7.35 (d, 2H), 7.08 (s, 4H), 6.87 (d, 2H), 4.33 (t, 4H, J = 4.70 Hz), 4.19-4.16 (m, 12H), 3.68 (t, 4H, J = 4.71 Hz), 3.69-3.66 (m, 12H), 3.63-3.59 (m, 36H), 3.53-3.49 (m, 36H), 3.34 (s, 18H); ^{13}C NMR ($CDCl_3$): δ (ppm) =167.43, 154.22, 152.57, 141.66, 129.61, 126.73, 125.48, 107.42, 106.05, 72.45, 71.99, 70.74, 70.60, 69.79, 69.16, 59.08; UV-visible ($CHCl_3$): λ_{max} (ε) = 326 nm (5,417), 312 nm (8,509), 296 nm (13,577), 285 nm (13,287 $M^{-1}cm^{-1}$); HRMS

(ESI): calcd for [*M* +Na+H]$^+$: 1450.7223; found: 1450.7222; Elemental analysis: cald. For $C_{70}H_{110}N_2O_{28}$, C- 58.89, H- 7.77, N- 1.96, found C- 58.70, H- 7.72, N- 1.92

Additional Figures:

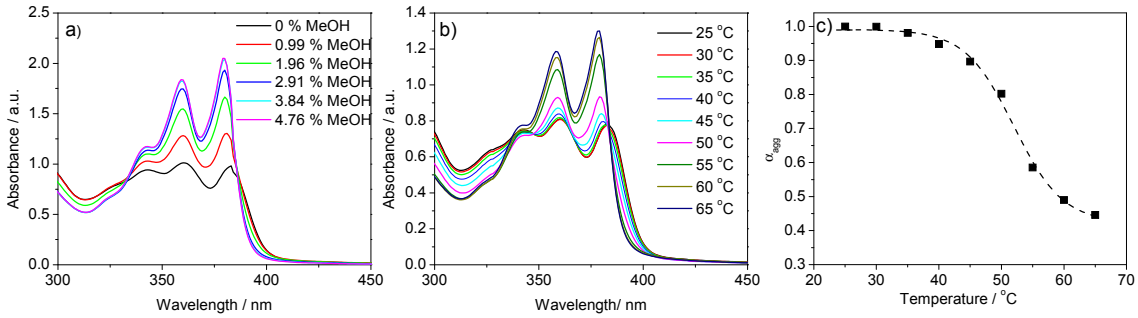


Fig S1: a) Variation of UV/vis spectra of **NDI-1** in 95: 5 MCH/ $CHCl_3$ as a result of MeOH addition. Concentration = 0.1 mM and temperature = 25°C; b) Variable-temperature UV/vis spectra of **NDI-1** in 95: 5 MCH/ $CHCl_3$; c) Variation of α_{agg} with temperature (the data from **Fig S1b** has been used to calculate the α_{agg} in each temperature using Equation 2 as described above.

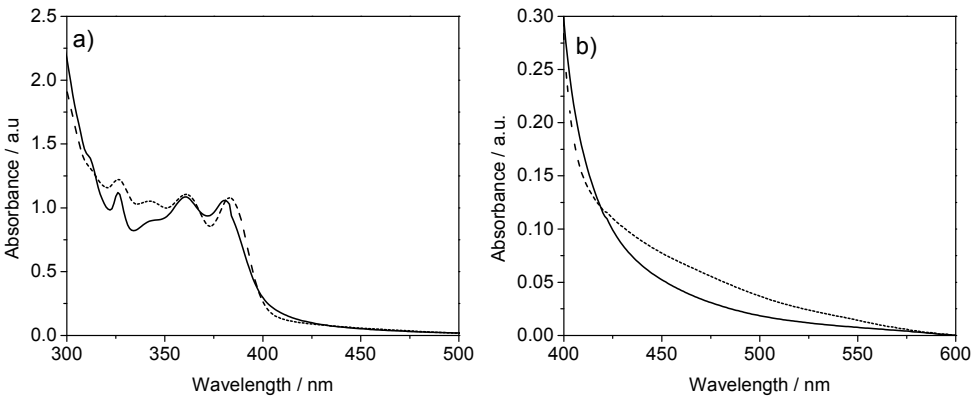


Fig S2: a) UV/vis spectra of **NDI-1** + **DAN-1** (solid line) and mathematical sum-spectra of the individual chromophores (dashed line); b) CT-region of the same spectra. Individual concentration of each chromophore = 0.1 mM, solvent- 95: 5 MCH/ $CHCl_3$, path-length of the cuvette = 1 cm

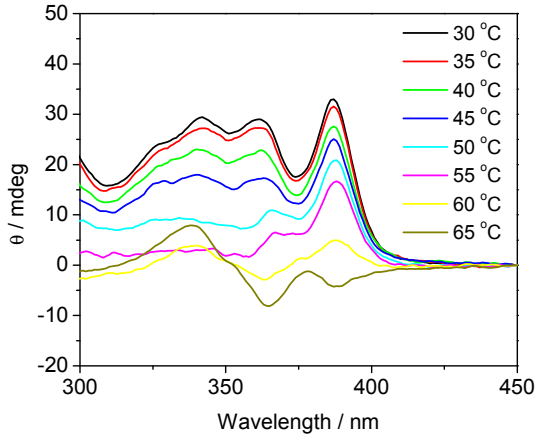


Fig S3: a) Variation of CD spectra of **NDI-1** + **DAN-1** (1:1) as a function of temperature. Individual concentration of each chromophore = 0.5 mM, solvent- 95: 5 MCH/ $CHCl_3$, path-length of the cuvette = 1 mm. The origin of slightly unusual CD-pattern at 65°C is not clear to us at this moment. Detail investigations are underway.

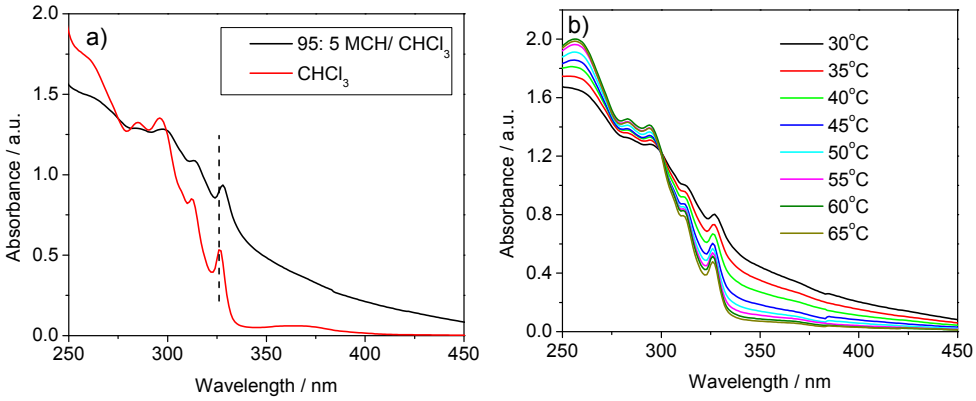


Fig S4: a) UV/vis spectra of **DAN-2** (concentration= 0.1 mM, T = 25 °C) in $CHCl_3$ and 95: 5 MCH/ $CHCl_3$; b) Variable temperature UV/vis spectra of **DAN-2** (concentration= 0.1 mM) in 95: 5 MCH/ $CHCl_3$. path-length of the cuvette = 1 cm

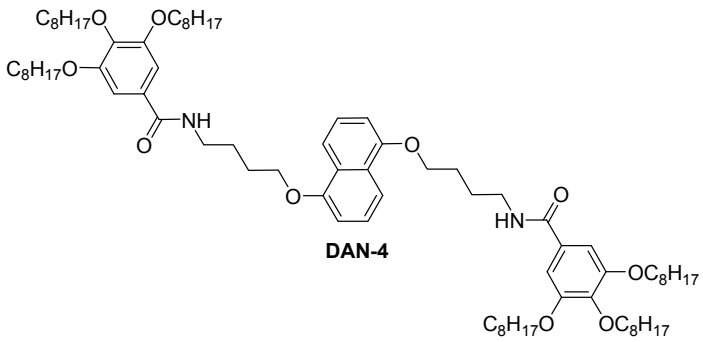


Fig S5: Structure of the control molecule **DAN-4**[5]

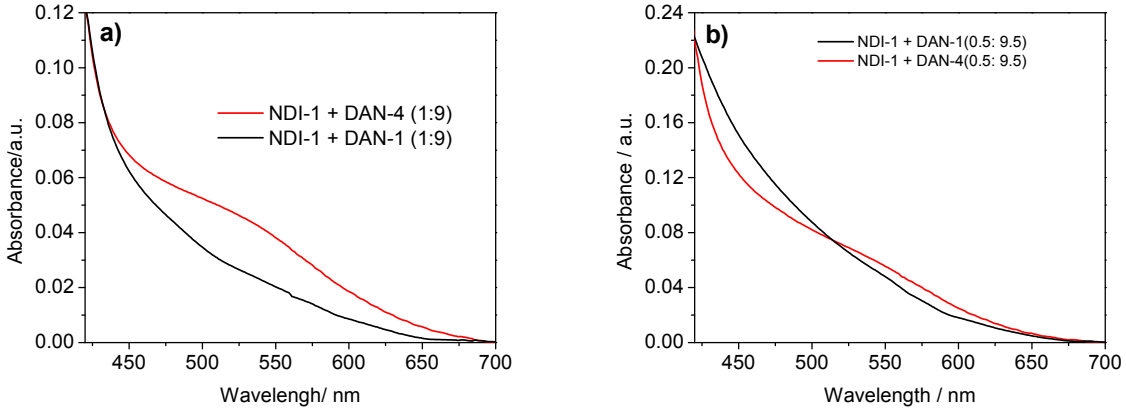


Fig S6: UV/vis spectra (CT-region) of (**NDI-1** + **DAN-1)** and (**NDI-1** + **DAN-4**) pairs at room temperature in various ratios (10 % NDI in left and 5 % NDI in right). Total chromophore concentration = 1 mM, path-length of the cuvette = 5 mm, and solvent = MCH/ $CHCl_3$ (95:5).

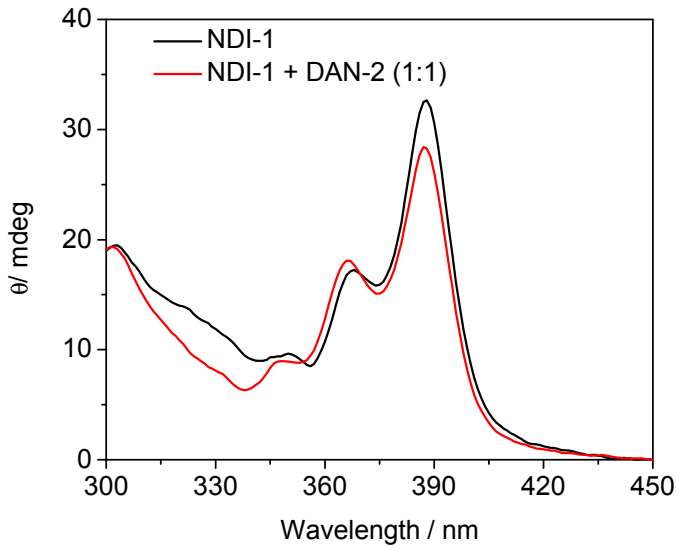


Fig S7: CD spectra of **NDI-1** and **NDI-1** + **DAN-2** (1: 1) in 95: 5 MCH/ $CHCl_3$. Individual concentration of each chromophore = 0.5 mM, T = 30 °C, path-length of the cuvette = 1 mm

References

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