**Supporting Information for:**

# Combined Transparency and Optical Nonlinearity Enhancement in Flexible Covalent Multimers by Operating Through-Space Interactions between Dipolar Chromophores

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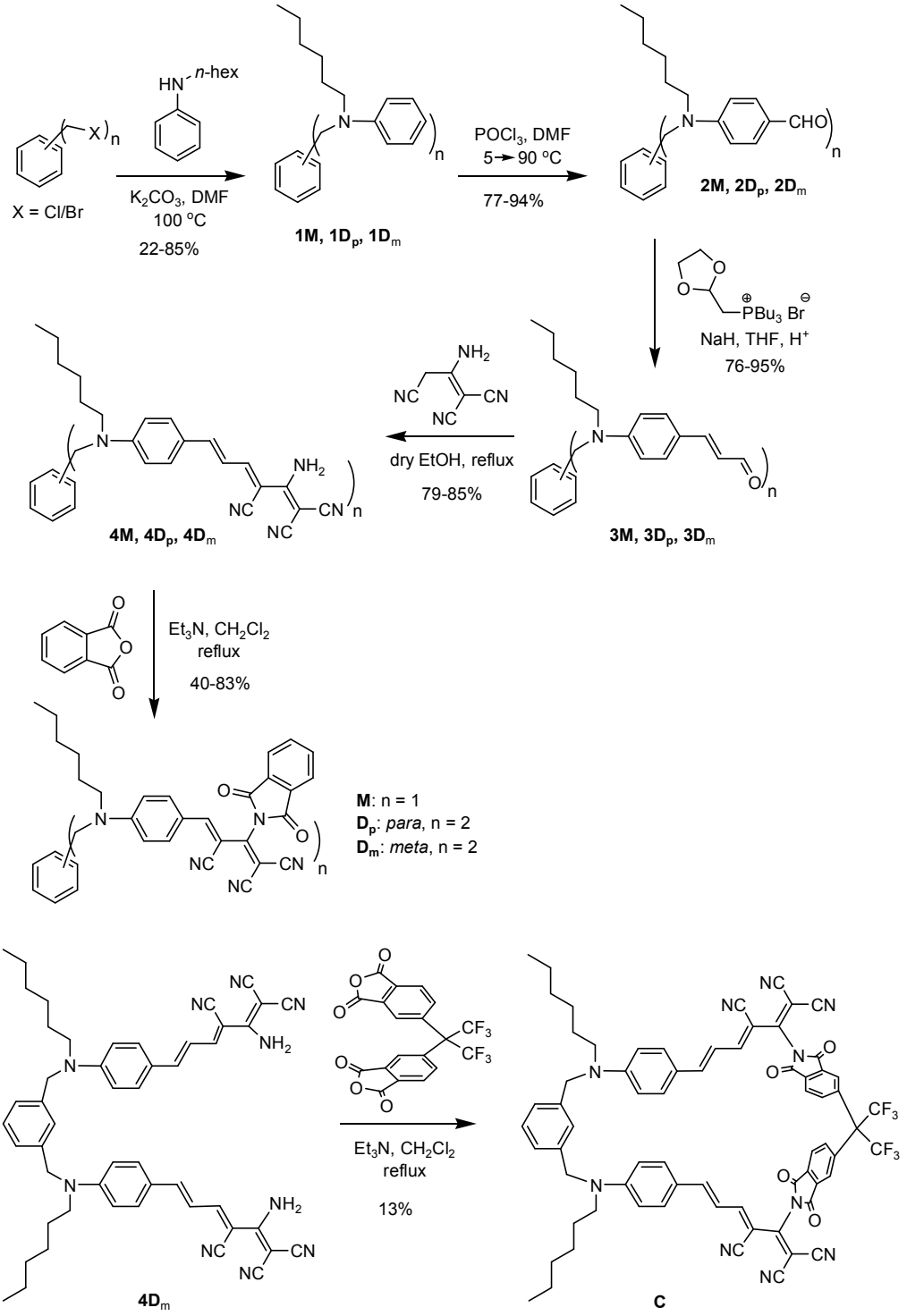
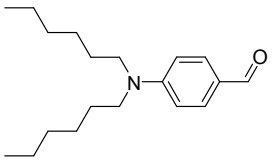
# Synthesis

***Scheme S1*. General Synthetic Strategy for Preparation of Multichromophores.**



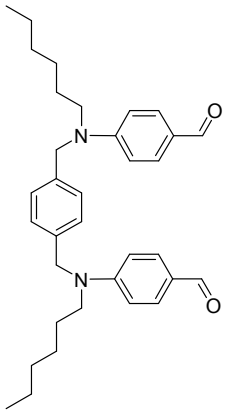
**Preparation of Aldehydes 2 via Vilsmeyer Haack Formylation:**

**Synthesis of 2M:**[1]



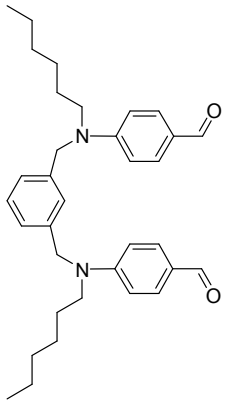

The required amount of $POCl_3$ (2.67 mL, 28.5 mmol) was slowly added to anhydrous *N,N*-dimethylformamide (40.0 mL) under ice-cold conditions (0-5 °C). After stirring the mixture for 15 min at the same temperature, it was heated briefly at 50 °C and again cooled to 5 °C to form the Vilsmeyers reagent. To the reagent formed, was added a solution of **1M** (5.0 g, 19.0 mmol) in DMF (15.0 mL) dropwise under cooling. The ice-bath was removed and the reaction mixture was stirred further for 30 min at room temperature and then heated to 90 °C for overnight. After the duration of the reaction, the reaction mixture was cooled to room temperature, poured into crushed ice. The solution was neutralized with NaOH (2M) and the organic contents were extracted using dichloromethane. After usual work up, the crude solid was then purified by silica-gel column chromatography using dichloromethane and heptane mixtures as the eluent. The collected fractions were evaporated to give viscous yellow oil in 77% yield. $^1$H NMR (200.13 MHz, $CDCl_3$) $\delta$ 0.93 (t, $J$ = 6.4 Hz, 6H), 1.27 (m, 12H), 1.55 (m, 4H), 3.28 (t, $J$ = 7.2 Hz, 4H), 6.57 (d, $J$ = 8.7 Hz, 2H), 7.62 (d, $J$ = 8.7 Hz, 2H), 9.62 (s, 1H); $^{13}$C NMR (50.32 MHz, $CDCl_3$) $\delta$ 14.0, 22.6, 26.7, 27.1, 31.6, 51.1, 110.6, 124.4, 132.2, 152.5, 189.9.

**Synthesis of $2D_p$:**




The Vilsmeyers formylating reagent (0.2 mL of $POCl_3$ in 7.0 mL of DMF) was initially prepared under ice-cold conditions. This reagent was briefly heated to 50 °C and then cooled to 5 °C. To the above reagent was added a solution of compound **$1D_p$** (0.46 g, 1.0 mmol) in DMF (1.7 mL) dropwise under ice-cold conditions. After the addition, the cooling bath was removed and the solution was allowed to stir at room temperature for 30 min. Later, again, the reaction mixture was heated at 70-90 °C for 2h. After heating, the solution was cooled and poured into crushed ice. This aqueous portion was neutralized with 4M NaOH solution, and the organic contents were extracted using dichloromethane/ether (3 × 25 mL). The combined organic extracts were washed with water, brine, dried over $Na_2SO_4$, filtered and then the solvent was evaporated to give a crude product which was further purified by a silica-gel column chromatography to afford a pale yellow solid 0.48 g (94%); mp 97-98 °C; IR (neat, $cm^{-1}$) 2735, 1656; $^1H$ NMR (200.13 MHz, $CDCl_3$) $\delta$ 0.89 (t, $J$ = 6.4 Hz, 6H), 1.27 (m, 12H), 1.63 (m, 4H), 3.48 (t, $J$ = 6.3 Hz, 4H), 4.62 (s, 4H), 6.67 (d, $J$ = 8.5 Hz, 4H), 7.13 (s, 4H), 7.68 (d, $J$ = 8.5 Hz, 4H), 9.71 (s, 2H); $^{13}C$ NMR (200.13 MHz, $CDCl_3$) $\delta$ 14.0, 22.6, 26.7, 27.0, 31.6, 51.6, 53.9, 111.2, 125.3, 126.7, 132.1, 136.4, 153.0, 190.1.

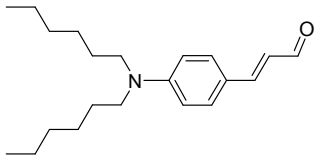
**Synthesis of $2D_m$:**




The Vilsmeyers formylating reagent (1.39 mL of $POCl_3$ in DMF 48.0 mL) which was initially prepared under ice-cold conditions was briefly heated to 50 °C and then cooled to 5 °C. To this reagent was added a solution of compound **$1D_m$** (3.20 g, 7.0 mmol) in DMF (12.0 mL) was added dropwise under ice-cold conditions. After the addition, the cooling bath was removed and the solution was allowed to stir at room temperature for 30 min. The reaction mixture was then heated at 70-90 °C for 2h. After the appropriate reaction time, the solution was cooled and poured into crushed ice. The aqueous portion was neutralized with 4M NaOH solution. The organic contents were extracted using dichloromethane/ether. The combined organic extracts were washed with water, brine, dried over $Na_2SO_4$, and filtered. The solvent was evaporated to give a crude product which was further purified by a silica-gel column chromatography to yield a yellow viscous liquid (3.32 g, 93%). IR (neat, $cm^{-1}$) 2730, 1666; $^1H$ NMR (200.13 MHz, $CDCl_3$) $\delta$ 0.89 (t, $J$ = 6.5 Hz, 6H), 1.27 (m, 12H), 1.56 (m, 4H), 3.35 (t, $J$ = 7.8 Hz, 4H), 4.59 (s, 4H), 6.59 (d, $J$ = 9.0 Hz, 4H), 6.88 (s, 1H), 7.07 (d, $J$ = 7.4 Hz, 2H), 7.32 (t, $J$ = 7.1 Hz, 1H), 7.64 (d, $J$ = 9.0 Hz, 4H), 9.7 (s, 2H); $^{13}C$ NMR (50.35 MHz, $CDCl_3$) $\delta$ 14.0, 22.6, 26.6, 27.0, 31.5, 51.6, 54.0, 111.1, 123.7, 125.1, 125.2, 129.3, 132.0, 137.9, 152.9, 190.0.

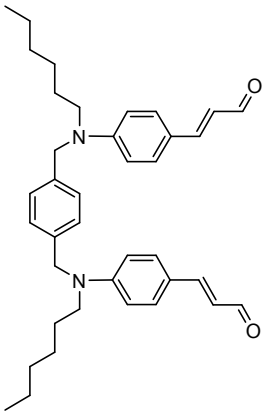
**General Procedure for the Synthesis of Vinylogated Aldehydes 3 by Spangler's Method:** A typical procedure for the synthesis of **3M** is described below as a representative case.

**Synthesis of 3M:**



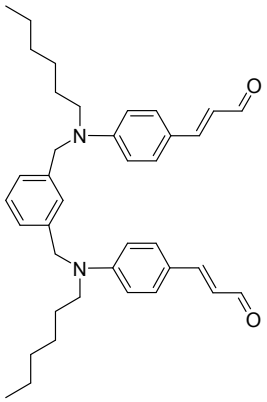

To a solution of the mixture of aldehyde **2M** (1.0 mmol) and tributyl-[1,3]-dioxolan-2-ylmethylphosphonium bromide[2] (1.1 mmol) in anhydrous tetrahydrofuran was added sodium hydride (60% dispersed in mineral oil, 3.0 mmol) under argon gas atmosphere and the resulting turbid solution was stirred at room temperature for 13 h. The reaction was monitored by TLC. After completion of the reaction, the excess NaH was quenched using 1N HCl solution under cooling and the reaction mixture was brought to acidic pH. The reaction mixture was stirred further more at room temperature for 4-5 h. The contents in the reaction flask were concentrated and the organic contents were extracted into ethyl acetate. The organic layer was washed with water followed by brine, dried over anhydrous $Na_2SO_4$, filtered and evaporated to dryness to afford the crude aldehyde which after purification by silica-gel column chromatography using dichloromethane gave the desired vinyl-homologated product **3M** as a yellow liquid. Yield: 76%. IR (neat) 1665 $cm^{-1}$; $^1H$ NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.93 (t, $J$ = 6.5 Hz, 6H), 1.36 (m, 12H), 1.61 (m, 4H), 3.31 (t, $J$ = 7.5 Hz, 4H), 6.51 (dd, $J_1$ = 15.5 Hz, $J_2$ = 7.9 Hz, 1H), 6.65 (d, $J$ = 9.0 Hz, 2H), 7.30-7.49 (m, 3H), 9.61 (d, $J$ = 7.9 Hz, 1H); $^{13}C$ NMR (75.47 MHz, $CDCl_3$) $\delta$ 13.1, 14.5, 27.2, 27.6, 32.1, 51.5, 111.7, 122.2, 123.6, 131.2, 150.2, 155.1, 194.2; HRMS ($LSIMS^+$, mNBA) calcd for $C_{21}H_{33}NO$ ($M^{+\cdot}$) *m/z* 315.2562, found 315.2561.

**Synthesis of $3D_p$:**




This compound was prepared readily by following the general procedure described above. In contrast, sodium hydride (60% dispersed in mineral oil, 0.17 g, 7.02 mmol) was added to a solution of tributyl-[1,3]-dioxolan-2-ylmethylphosphonium bromide[2] (0.96 g, 2.57 mmol) and the aldehyde **$2D_p$** (0.60 g, 1.17 mmol) in anhydrous tetrahydrofuran (40.0 mL) under argon gas atmosphere. Isolation and purification as above afforded the deep yellow solid **$3D_p$** in good yield. Yield: 83%; mp 118-119 °C; IR (neat, $cm^{-1}$) 2725, 1665; $^1H$ NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.90 (t, $J$ = 7.0 Hz, 6H), 1.29-1.35 (m, 12H), 1.63-1.72 (m, 4H), 3.44 (t, $J$ = 7.5 Hz, 4H), 4.59 (s, 4H), 6.52 (dd, $J_1$ = 15.9 Hz, $J_2$ = 7.8 Hz, 2H), 6.65 (d, $J$ = 9.0 Hz, 4H), 7.14 (s, 4H), 7.35 (d, $J$ = 15.9 Hz, 2H), 7.40 (d, $J$ = 9.0 Hz, 4H), 9.58 (d, $J$ = 7.8 Hz, 2H); $^{13}C$ NMR (75.47 MHz, $CDCl_3$) $\delta$ 14.0, 22.6, 26.7, 27.1, 31.6, 51.5, 53.9, 111.8, 121.7, 123.7, 126.7, 130.6, 136.6, 150.8, 153.7, 193.7.

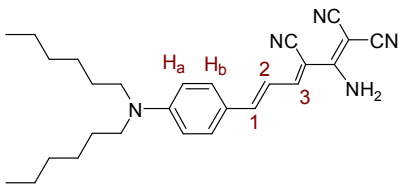
**Synthesis of $3D_m$:**



This compound was prepared by following the procedure described for **$3D_p$**. To a solution of tributyl-[1,3]-dioxolan-2-ylmethylphosphonium bromide[2] (0.86 g, 2.34 mmol) and the aldehyde **$2D_p$** (0.50 g, 0.98 mmol) in anhydrous tetrahydrofuran (30.0 mL) under argon gas atmosphere, sodium hydride (60% dispersed in mineral oil, 0.14 g, 5.85 mmol) was introduced. Isolation and purification as above afforded the deep yellow compound **$3D_p$** in good yield. Yellow solid; yield: 95%; mp 87-89 °C; IR (neat, $cm^{-1}$) 2748, 1661; $^1H$ NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.88 (t, $J$ = 6.9 Hz, 6H), 1.22-1.40 (m, 12H), 1.55-1.70 (m, 4H), 3.33 (t, $J$ = 7.5 Hz, 4H), 4.56 (s, 4H), 6.51 (dd, $J_1$ = 15.9 Hz, $J_2$ = 7.8 Hz, 2H), 6.56 (d, $J$ = 9.0 Hz, 4H), 6.90 (s, 4H), 7.07 (d, $J$ = 7.8 Hz, 2H), 7.27-7.38 (m, 7H), 9.58 (d, $J$ = 8.1 Hz, 2H); $^{13}C$ NMR (75.47 MHz, $CDCl_3$) $\delta$ 14.0, 22.7, 26.7, 27.2, 31.6, 51.7, 54.2, 111.8, 121.8, 123.8, 123.9, 125.1, 129.2, 130.6, 138.3, 150.8, 153.7, 193.7.

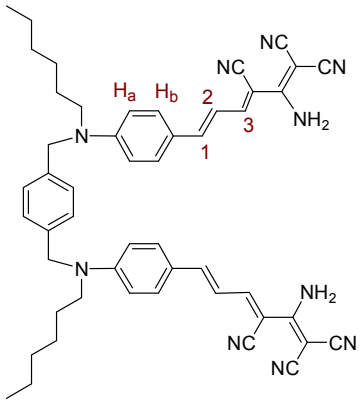
**General Procedure for the Preparation of Amines 4 from 3 by Knoevenagel Condensation:** A typical procedure for the synthesis of **4M** is provided below as a representative case.

**Synthesis of 4M:**



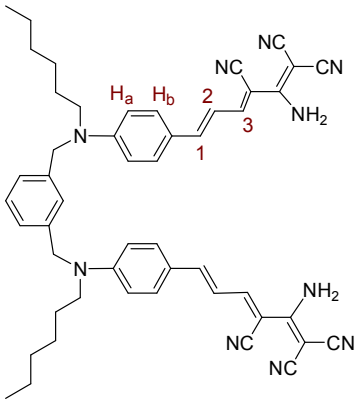

To a solution of the aldehyde **3M** (2.39 mmol) in absolute ethanol (2.0 mL), was added a solution of 3-amino-2-cyano-pent-2-endiamine[3] (2.39 mmol) in absolute ethanol (2.0 mL). The resulting solution was refluxed for appropriate time until the starting compound was consumed completely as monitored by TLC. After the reaction time, the reaction mixture was cooled to room temperature, concentrated under vacuum. The crude residue thus obtained was further purified by silica-gel column chromatography using dichloromethane as the eluent. The collected fractions were evaporated under reduced pressure and dried to afford the desired compound **4M** in good yields. Yield: 85%; mp 168-170 °C; IR (neat, $cm^{-1}$) 2212; $^1H$ NMR (500.13 MHz, $CDCl_3$) $\delta$ 0.91 (t, $J$ = 6.5 Hz, 6H), 1.34 (m, 12H), 1.62 (m, 4H), 3.35 (t, $J$ = 7.5 Hz, 4H), 5.96 (bs, 2H), 6.63 and 7.48 (AA'XX', $J_{AX}$ = 9.0 Hz, 2H, $H_a$, $H_b$), 7.03 (dd, $J_{12}$ = 14.7 Hz, $J_{23}$ = 11.7 Hz, 1H, $H_2$), 7.26 (d, $J_{12}$ = 14.7 Hz, 1H, $H_1$), 8.08 (d, $J_{23}$ = 11.7 Hz, 1H, $H_3$); $^{13}C$ NMR (75.47 MHz, $CDCl_3$) $\delta$ 14.1, 22.7, 26.7, 27.3, 31.6, 51.3, 94.4, 111.8, 115.0, 115.3, 115.5, 117.3, 121.8, 132.4, 151.7, 153.4, 155.9, 163.8; HRMS (LSIMS$^+$, mNBA) calcd for $C_{27}H_{35}N_5$ $(M + H)^+$ *m/z* 430.2971, found 430.2952. Elemental analysis (%) for $C_{27}H_{35}N_5$: calcd.: C, 75.49; H, 8.21; N, 16.30; found: C, 74.98; H, 8.05; N, 15.84.

**Synthesis of $4D_p$:**




This compound was prepared and isolated by following the general procedure described above. In this case, the solution of aldehyde **$3D_p$** (0.20 g, 0.35 mmol) in absolute ethanol was added to a solution of 3-amino-2-cyano-pent-2-endiamine[3] (0.12 g, 0.89 mmol) in absolute ethanol and heated at reflux for a period of 60 h. Purification by silica-gel column chromatography using methanol and dichloromethane mixture (1:9) as the eluent provided a red solid. Yield: 79%; mp 226-228 (dec.); IR (neat, $cm^{-1}$) 3338, 2212; $^1H$ NMR (300.13 MHz, $CDCl_3$ + $CD_3OD$) $\delta$ 0.85 (t, $J$ = 6.6 Hz, 6H), 1.22-1.40 (m, 12H), 1.60-1.80 (m, 4H), 3.44 (t, $J$ = 7.0 Hz, 4H), 4.60 (s, 4H), 6.63 and 7.41 (AA'XX', $J_{AX}$ = 9.0 Hz, 8H, $H_a$, $H_b$), 6.99 (dd, $J_{12}$ = 14.8 Hz, $J_{23}$ = 11.4 Hz, 2H, $H_2$), 7.10 (s, 4H), 7.20 (d, $J_{12}$ = 14.8 Hz, 2H, $H_1$), 7.72 (d, $J_{23}$ = 11.4 Hz, 2H, $H_3$); $^{13}C$ NMR (75.47 MHz, $CDCl_3$ + $CD_3OD$) $\delta$ 14.1, 22.8, 26.9, 27.4, 31.8, 50.0, 51.9, 54.2, 96.8, 112.4, 115.0, 115.4, 116.0, 118.0, 122.8, 127.0, 131.8, 136.7, 151.8, 155.8, 165.4; HRMS (ESI) calcd for $C_{50}H_{52}N_{10}Na$ $(M + Na)^+$ *m/z* 815.4274 found: 815.4277. Elemental analysis (%) for $C_{50}H_{52}N_{10}$: calcd.: C, 75.73; H, 6.61; N, 17.66; found: C, 75.64; H, 6.67; N, 17.10.

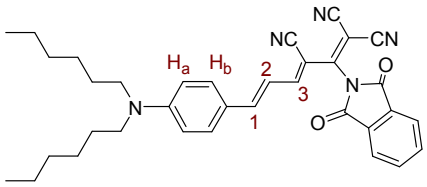
**Synthesis of $4D_m$:**




This compound was prepared and isolated by following the general procedure described above. For this, the solution of aldehyde **$3D_m$** (0.20 g, 0.35 mmol) and 3-amino-2-cyano-pent-2-endiamine[3] (0.12 g, 0.89 mmol) in absolute ethanol was heated at reflux. After the appropriate reaction time, purification using ethyl acetate and dichloromethane mixtures (1:4) afforded a deep-red solid. Yield: 85%; mp 142-145 °C ; IR (neat, $cm^{-1}$) 3323, 2211; $^1H$ NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.87 (t, $J$ = 7.5 Hz, 6H), 1.25-1.40 (m, 12H), 1.50-1.70 (m, 4H), 3.34 (t, $J$ = 7.5 Hz, 4H), 4.58 (s, 4H), 6.19 (s, 4H), 6.44 and 7.27 (AA'XX', $J_{AX}$ = 9.0 Hz, 8H, $H_a$, $H_b$), 6.77 (s, 1H), 7.01 (dd, $J_{12}$ = 15.0 Hz, $J_{23}$ = 12.0 Hz, 2H, $H_2$), 7.12 (d, $J$ = 6.0 Hz, 2H), 7.24 (d, $J_{12}$ = 15.0 Hz, 2H, $H_1$), 7.35 (t, $J$ = 6.0 Hz, 1H), 8.01 (d, $J_{23}$ = 12.0 Hz, 2H, $H_3$); $^{13}C$ NMR (75.47 MHz, $CDCl_3$) $\delta$ 14.1, 22.7, 26.7, 27.5, 31.6, 50.9, 52.0, 54.2, 95.7, 112.0, 115.0, 115.1, 115.6, 117.7, 122.5, 123.4, 125.5, 129.4, 131.8, 137.8, 151.5, 152.7, 155.7, 164.1; HRMS (ESI) calcd for $C_{50}H_{52}N_{10}Na$ $(M + Na)^+$ *m/z* 815.42741 found: 815.4272; Elemental analysis (%) for $C_{50}H_{52}N_{10}.1.15$ ($C_2H_6O$): calcd.: C, 74.25; H, 7.02; N, 16.56; found: C, 74.29; H, 7.04; N, 16.49.

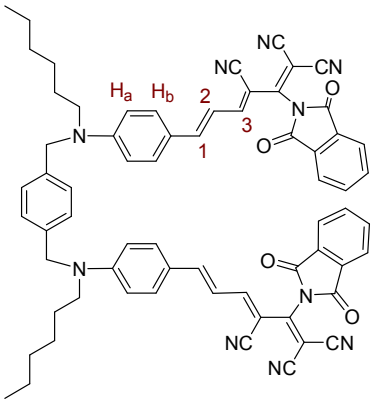
**General Procedure for the Preparation of Phthalimides M, $D_p$ and $D_m$ via Condensation:** A typical procedure for the synthesis of **4M** is provided below as a representative case.

**Synthesis of M:**



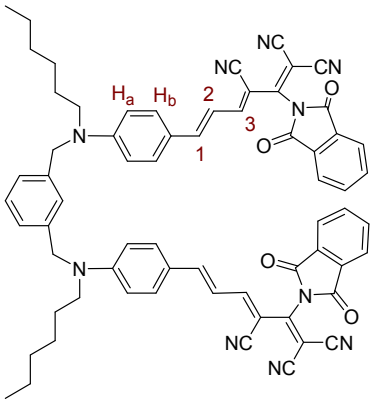

To a well stirred solution of the mixture of chromophore **4M** (0.44 mmol, 1.0 equiv.) and phthalic anhydride (1.32 mmol, 3.0 equiv.) in dry dichloromethane (12.0 mL) was introduced triethylamine (1.32 mmol, 3.0 equiv.) under argon gas atmosphere. The reaction mixture was stirred at room temperature for a period of 1-12 h. The reaction was monitored by TLC from time to time. After appropriate reaction time, the reaction mixture was concentrated at the rotary evaporator and the resulting crude residue was subjected to silica-gel column chromatography using dichloromethane as the eluent. The fractions were combined, evaporated and dried to afford the desired pure compound in good yields. Yield: 83%; mp 182-184 °C; IR (neat, $cm^{-1}$) 2214 $cm^{-1}$; $^1H$ NMR (500.13 MHz, $CDCl_3$) $\delta$ 0.92 (t, $J$ = 6.5 Hz, 6H), 1.34 (m, 12H), 1.64 (m, 4H), 3.40 (t, $J$ = 7.5 Hz, 4H), 6.65 and 7.54 (AA'XX', $J_{AX}$ = 9.0 Hz, 4H, $H_a$, $H_b$), 7.17 (dd, $J_{12}$ = 14.3 Hz, $J_{23}$ = 12.2 Hz, 1H, $H_2$), 7.39 (d, $J_{12}$ = 14.3 Hz, 1H, $H_1$), 7.87 and 8.02 (AA'XX', 4H), 7.93 (d, $J_{23}$ = 12.2 Hz, 1H, $H_3$); $^{13}C$ NMR (75.47 MHz, $CDCl_3$) $\delta$ 14.4, 23.0, 27.1, 27.8, 32.0, 51.9, 98.2, 112.9, 113.0, 115.0, 119.5, 123.3, 125.4, 131.7, 135.0, 135.9, 152.0, 153.4, 155.8, 156.4, 164.5; HRMS ($LSIMS^+$, mNBA) calcd for $C_{35}H_{37}N_5O_2$ ($M^{+\cdot}$) *m/z* 559.2947, found 559.2941. Elemental analysis (%) for $C_{35}H_{37}N_5O_2$: calcd.: C, 75.11; H, 6.66; N, 12.51; found: C, 75.39; H, 7.06; N, 12.47.

**Synthesis of $D_p$:**



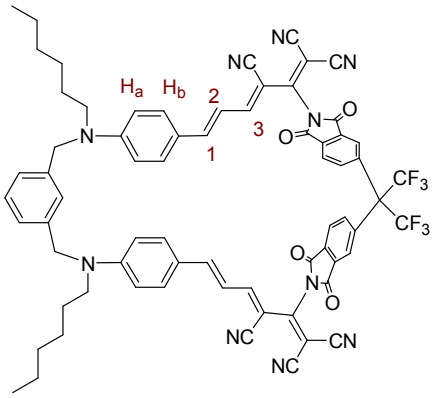

This compound was synthesized by following the general procedure described above. But, the condensation partners were **4D$_p$** (0.08 g, 0.11 mmol) and phthalic anhydride (0.09 g, 0.65 mmol) in dry dichloromethane (3.0 mL) in the presence triethylamine (90.0 µL, 0.65 mmol). Purification by silica-gel column chromatography using dichloromethane afforded a violet-blue solid **D$_p$**. Yield: 40%; IR (neat, $cm^{-1}$) 2216, 1736; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.90 (t, $J$ = 7.0 Hz, 6H), 1.20-1.40 (m, 12H), 1.60-1.80 (m, 4H), 3.51 (t, $J$ = 7.8 Hz, 4H), 4.67 (s, 4H), 6.69 and 7.51 (AA'XX', $J_{AX}$ = 9.0 Hz, 8H, $H_a$, $H_b$), 7.14 (s, 4H), 7.17 (dd, $J_{12}$ = 14.4 Hz, $J_{23}$ = 11.9 Hz, 2H, $H_2$), 7.38 (d, $J_{12}$ = 14.4 Hz, 2H, $H_1$), 7.89 and 8.04 (AA'XX', 8H), 7.97 (d, $J_{23}$ = 11.9 Hz, 2H, $H_3$); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 14.0, 22.6, 26.6, 27.3, 31.5, 51.9, 54.1, 98.8, 100.0, 112.5, 112.7, 114.3, 119.4, 123.4, 125.0, 126.8, 131.2, 133.5, 135.6, 136.0, 152.7, 153.0, 155.3, 155.8, 163.8; HRMS (ESI) calcd for $C_{66}H_{56}N_{10}O_4Na$ $(M+Na)^+$ *m/z* 1075.43837, found: 1075.4397. Elemental analysis (%) for $C_{66}H_{56}N_{10}O_4$ calcd.: C, 75.27; H, 5.36; N, 13.30; found: C, 75.03; H, 5.79; N, 12.91.

**Synthesis of $D_m$:**




This compound was synthesized by following the general procedure described above. The condensation partners were **4D$_m$** (0.06 g, 0.08 mmol) and phthalic anhydride (0.07 g, 0.45 mmol) in dry dichloromethane (2.5 mL) in the presence of triethylamine (63.0 μL). The crude product was purified by silica-gel column chromatography using ethyl acetate and dichloromethane mixtures (2:98) afforded a green-blue solid **D$_m$**. Yield: 60%; IR (neat, $cm^{-1}$) 2216, 1736; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.87 (t, $J$ = 7.5 Hz, 6H), 1.20-1.50 (m, 12H), 1.55-1.75 (m, 4H), 3.38 (t, $J$ = 7.5 Hz, 4H), 4.63 (s, 4H), 6.53 and 7.38 (AA'XX', $J_{AX}$ = 9.0 Hz, 8H, $H_a$, $H_b$), 6.80 (s, 1H), 7.12 (d, $J$ = 8.0 Hz, 2H), 7.13 (dd, $J_{12}$ = 14.4 Hz, $J_{23}$ = 11.7 Hz, 2H, $H_2$), 7.28 (d, $J_{12}$ = 14.4 Hz, 2H, $H_1$), 7.36 (t, $J$ = 8.0 Hz, 1H), 7.88 and 8.02 (AA'XX', 8H), 7.98 (d, $J_{23}$ = 11.7 Hz, 2H, $H_3$); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 14.0, 22.6, 26.6, 27.4, 31.5, 52.0, 54.3, 98.7, 112.5, 112.6, 112.7, 114.4, 119.4, 123.3, 123.4, 125.0, 125.7, 129.7, 131.2, 133.3, 135.6, 137.4, 152.7, 152.8, 155.2, 156.0, 163.9; HRMS (ESI) calcd for $C_{66}H_{56}N_{10}O_4Na$ $(M + Na)^+$ *m/z* 1075.4383 found: 1075.4378; Elemental analysis (%) for $C_{66}H_{56}N_{10}O_4$ calcd.: C, 75.27; H, 5.36; N, 13.30; found: C, 75.46; H, 5.80; N, 12.85.

**Synthesis of Macrocycle, C:**




The solution of **4D$_m$** (0.025g, 0.024 mmol) and 4,4'-(hexafluoroisopropylidene)bisphthalic anhydride (0.032 g, 0.071 mmol) in dry dichloromethane (50.0 mL) was added a solution of triethylamine in dichloromethane (30.0 mL) slowly dropwise for a period of 40 min with continous stirring. After the addition, the solution was heated to reflux at 60 °C for a duration of 60 h. The color of the reaction mixture turned from blood-red to purple to blue. When the starting compound was found to complete by TLC, the reaction mixture was cooled to room temperature, concentrated at the rotary evaporator. The residue obtained was subjected to flash column chromatography using 5% ethyl acetate in 95% dichloromethane. The pure product thus procured was recrystallized from dichloromethane and heptane mixtures to afford a deep blue shiny solid **C**. Yield: 13%; IR (neat, $cm^{-1}$) 2215, 1736; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.89 (t, $J$ = 7.8 Hz, 6H), 1.10-1.40 (m, 12H), 1.45-1.75 (m, 4H), 3.30-3.50 (m, 4H), 4.63 (s, 4H), 6.50 (d, $J$ = 9.0 Hz, 4H, $H_a$), 6.80 (s, 1H), 7.10 (d, $J$ = 7.8 Hz, 2H), 7.19 (dd, $J_{12}$ = 14.3 Hz, $J_{23}$ = 11.7 Hz, 2H, $H_2$), 7.28-7.45 (m, 7H), 7.64 (d, $J_{23}$ = 11.7 Hz, 2H, $H_3$), 7.71 (m, 2H), 8.15-8.25 (m, 4H); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 14.0; 22.6, 26.6, 27.5, 29.7, 31.5, 52.4, 53.4, 54.6, 98.5, 111.7, 112.6, 112.7, 113.9, 119.4, 122.6, 123.5, 125.6, 125.8, 126.6, 129.7, 131.6, 131.9, 133.4, 133.6, 136.4, 137.5, 140.4, 151.5, 152.9, 155.6, 155.7, 162.3, 163.4; HRMS (ESI) calcd for $C_{69}H_{55}N_{10}O_4F_6$ $(M + H)^+$ *m/z* 1201.4312 found: 1201.4336.

## HRS set-up

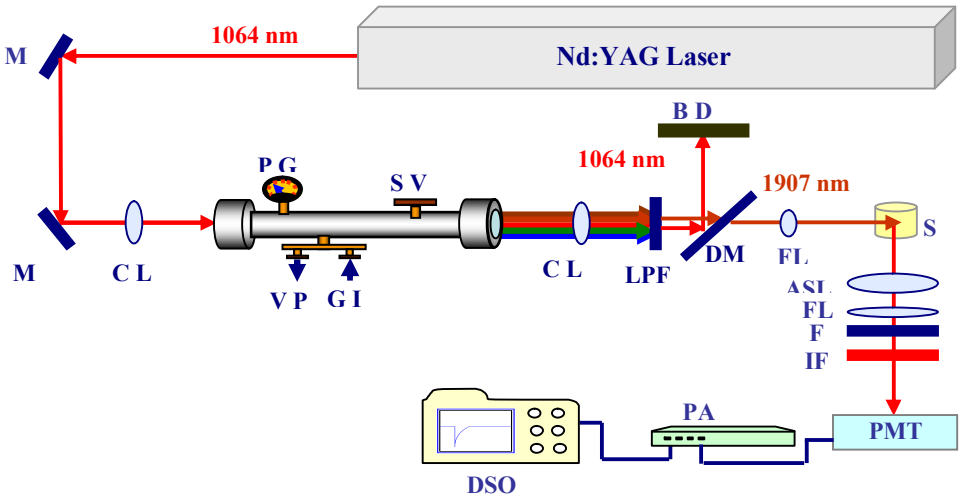



***Figure S1.*** Experimental set-up for the HRS measurement at 1907 nm. M-High energy laser mirror; CL-Collimating lens; PG-Pressure Gauge; SV-Safety Valve; VP-Vacuum Pump; GI-Gas Inlet; LPF-Long-pass filter; BD-Beam Dump; DM-Dichroic mirror; S-Sample; ASL-Aspherical Lens; FL-Focusing Lens; F-1907 cut-off filter; IF- Interference Filter; PMT-Photomultiplier Tube; PA-Preamplifier; DSO- Digital Storage Oscilloscope

## Two-level model for push-pull chromophores

The charge-resonance model for dipolar (push-pull) chromophores is based on a two-state description. The two resonant basis states (the neutral, *N*, and the zwitterionic, *Z*) are separated by an energy gap $2\eta$ and mixed by the charge resonance integral $-\sqrt{2}t$. The ground and excited state, $g = \sqrt{1-\rho}|N\rangle + \sqrt{\rho}|Z\rangle$ and $e = \sqrt{\rho}|N\rangle - \sqrt{1-\rho}|Z\rangle$, are defined by a single parameter, $\rho$, describing the degree of charge transfer in the ground state ($0 \le \rho \le 1$), univocally defined by $\eta$ and *t*:

$$\rho = \frac{1}{2}\left[1 - \frac{\eta}{\sqrt{\eta^2 + 2t^2}}\right] \qquad (1s)$$

Excitation energy, ground-state, excited-state and transition dipole moments can be expressed as functions of $\rho$:

$$\hbar\omega_{ge} = \sqrt{2}t\sqrt{\frac{1}{\rho(1-\rho)}}; \qquad \mu_{ge} = \mu_0\sqrt{\rho(1-\rho)} \qquad (2s)$$

where $\mu_0$ is the dipole moment of the zwitterionic basis state (the dipole moment of the neutral basis state is neglected). As a consequence, the static hyperpolarizability, $\beta(0)$, can be expressed as a function of $\rho$:

$$\beta_{zzz}(0) = \frac{3\mu_0^3[\rho(1-\rho)]^2(1-2\rho)}{4t^2} \qquad (3s)$$

where $\beta$ is expressed in the X convention, and *z* is the principal molecular axis.

***Table S1.*** Ground-state dipole moments and relative static HRS hyperpolarisabilities obtained by the theoretical modelling.

| | $\mu_z$ [D] | $\beta_0^{HRS}$ / ($N\beta_0^{HRS}$(M)) |
|---|---|---|
| **M** | 9.8 | 1 |
| **$D_p$** | 11.7 | 1.39 |
| **$D_m$** | 11.6 | 1.46 |
| **C** | 14.7 | 1.45 |

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