Electronic Supporting Information

Evidence of preferential π-stacking: a study of intermolecular and intramolecular charge transfer complexes.

N. S. Saleesh Kumar, Maneesh D. Gujrati and James N. Wilson

Contents page

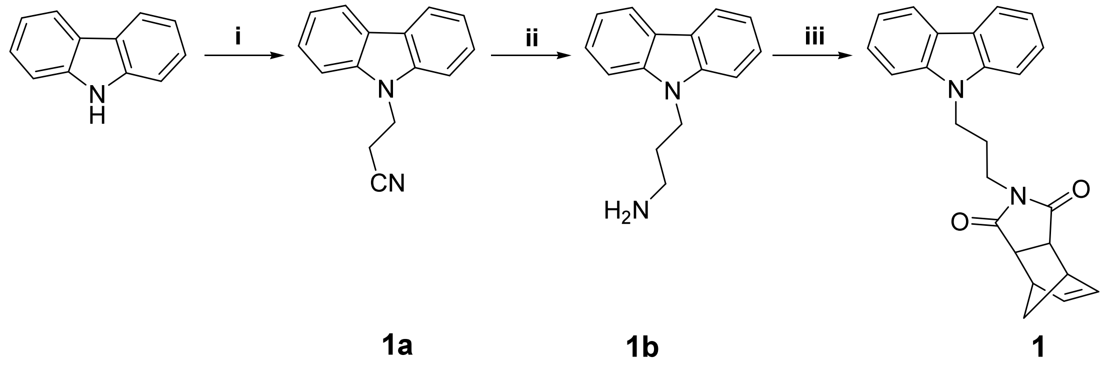
Reagents and Instruments:

The reagents and materials for synthesis were used as obtained from Sigma Aldrich and TCI America and used without further purification. ACS reagent grade solvents were obtained from EMD Chemicals. When necessary, dry solvents obtained from Sigma-Aldrich were used as described in the experimental procedures below. ^{1}H NMR spectra were recorded on Bruker 400 and 500 MHz spectrometer using tetramethylsilane (TMS) as the internal standard and chloroform-*d* ($CDCl_3$) as the solvent. Absorbance spectra were obtained on a Perkin-Elmer Lambda 35 UV-vis spectrometer. Fluorescence studies were performed on a Perkin-Elmer LS55 Fluorometer. For determination of Φ_{em} and K_{SV}, solutions were prepared to an optical density of 0.05 in CH_2Cl_2, in order to minimize inner filter effects. Perylene in cyclohexane was used as a reference for quantum yields.[1] Quantum yields were calculated according to the equation:

$$\frac{\Phi}{\Phi_R} = \frac{n^2}{n_R^2} \times \frac{\int F}{\int F_R} \times \frac{I_0(\lambda_{ex,\,S})}{I_0(\lambda_{ex,\,R})}$$

where the factor, $I_0(\lambda_{ex,\ S})/I_0(\lambda_{ex,\ R})$ is the correction for lamp intensities at the corresponding wavelengths.[2] The fluorescence lifetimes were obtained on a Frequency-Domain Lifetime Spectrometer ChronoFD from ISS exciting at 280 nm using terphenyl as a standard. Gel permeation chromatography was performed on a Waters 1525 HPLC equipped with a Waters 2998 PDA detector. Samples were monitored at 254 nm, 305 nm and 365 nm. A Waters Styragel column (HR 4E THF) was converted over to $CHCl_3$ following the manufacturer's procedure. Polystyrene (Polymer Standards Service-USA, Inc.) was used as a standard.

Synthesis and characterization of 1



Scheme: 1

Reagents and conditions: i) acrylonitrile, tetrabutyl ammonium hydroxide (40% in water); ii) $LiAlH_4$, diethyl ether; iii) *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride, DMF, 125 °C, 12h

Compound **1a** was synthesised according to the reported procedure.[3]

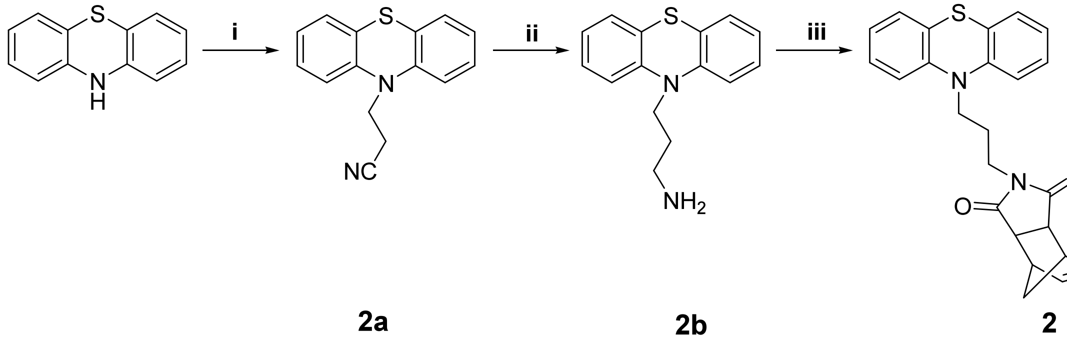
3-(9H-carbazol-9-yl)propan-1-amine (1b) This is a modified procedure of a previous report by Godefroi *et* al.[4] The nitrile **1a** (10 g, 45.43 mmol) was placed in a soxhlet extractor and was extracted into 250 mL of ether containing 10 g of $LiAlH_4$. After 72 h, the reaction mixture is quenched by the addition of ethyl acetate at 0 °C and the product was extracted using excess ethyl acetate. The solvent was evaporated off and the product **1b** was obtained as a white solid following purification by column chromatography using silica as the packing material and mixture of DCM and methanol (7:3) as the eluent. 68%; IR ν_{max}: 717, 744, 792, 886, 924, 952, 998, 1018, 1069, 1122, 1151, 1218, 1255, 1289, 1325, 1346, 1383, 1473, 1450, 1486, 1593, 2928 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):δ 1.57 (2H, s, broad), 2.02 (2H, m), 2.76 (2H, t, J = 7.5 Hz), 4.42 (2H, t, J = 7.5 Hz), 7.25 (2H, m), 7.46 (4H, m), 8.12 (2H, d, J = 10 Hz); ^{13}C NMR (100.57 MHz, $CDCl_3$): δ 32.9, 40.04, 40.88, 109.05, 109.11, 119.25, 120.78, 123.25, 126.07, 140.82; MS (FAB) calcd for $C_{15}H_{16}N_2$ ($M+H^+$). (225.13); found 225.

Monomer **1**: A suspension of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (502 mg, 3.05 mmol) in 10 mL of DMF was heated to 100 °C, after which compound **1b** was added quickly in argon atmosphere. The resulting mixture was heated at 125 °C for 12 h. The reaction mixture was poured into 250 mL of cold water and extracted using dichloromethane. The crude mixture was purified by column chromatography using silica as the packing material and mixture of hexane and DCM (3:7) as the eluent to yield the monomer **1** in 80% yield.

White powder. Mp: 180 °C; IR ν_{max}: 667, 720, 747, 783, 810, 888, 1008, 1055, 1122, 1130, 1153, 1175, 1231, 1328, 1345, 1376, 1402, 1456, 1469, 1488, 1599, 1696, 2942 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):δ 1.20 (1H, d, J = 10 Hz), 1.525 (1H, d, J = 10 Hz), 2.17 (2H, m), 2.16 (2H, s), 3.28 (2H, s), 3.63 (2H, t, J = 7.5 Hz), 4.37 (2H, t, J = 7.5 Hz), 6.29 (2H, s), 7.26 (2H, m), 7.40 (2H, d, J = 8 Hz), 7.48 (2H, m), 8.11 (2H, m); ^{13}C NMR (100.57

MHz, $CDCl_3$): δ 27.47, 37.1, 41.29, 43.17, 45.58, 48.18, 108.86, 119.48, 120.83, 123.39, 126.19, 138.19, 140.49, 178.22; MS (HRMS) calcd for $C_{24}H_{22}N_2O_2$ (M^+). (370.1681); found 370.1678.

Synthesis and characterization of **<u>2</u>**



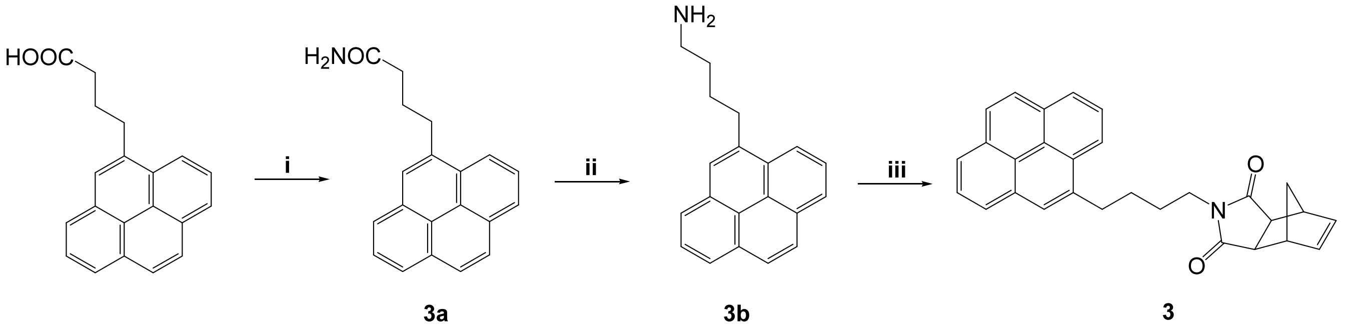
Scheme: 2

Reagents and conditions: i) acrylonitrile, tetrabutyl ammonium hydroxide (40% in water); ii) $LiAlH_4$, diethyl ether; iii) *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride, DMF, 125 °C, 12h

Compound **2a** and 2**b** was synthesised according to the reported procedures.[4,5] Monomer **2** was synthesised using the same procedure as that for monomer **1**.

White powder; 64%; Mp: 95 °C; IR ν_{max}: 665, 718, 752, 783, 891, 1015, 1131, 1253, 1287, 1339, 1390, 1455, 1573, 1594, 1693, 1773 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.17 (1H, d, J = 9.5 Hz), 1.52 (1H, d, J = 10 Hz), 2.10 (2H, m), 2.64 (2H, s), 3.24 (2H, s), 3.63 (2H, t, J = 7 Hz), 3.93 (2H, t, J = 10 Hz), 6.25 (2H, s), 6.85 (2H, d, J = 8 Hz), 6.95 (2H, t, J = 7.5 Hz), 7.16 (4H, d, J = 7.5 Hz); ^{13}C NMR (100.57 MHz, $CDCl_3$): δ 25.89, 36.96, 43.22, 45.37, 45.53, 48.23, 115.80, 123.09, 125.82, 127.69, 127.95, 138.18, 145.31, 178.33; MS (HRMS) calcd for $C_{24}H_{22}N_2O_2S$ (M^+). (402.1402); found 402.1399.

Synthesis and characterization of **<u>3</u>**



Scheme: 3

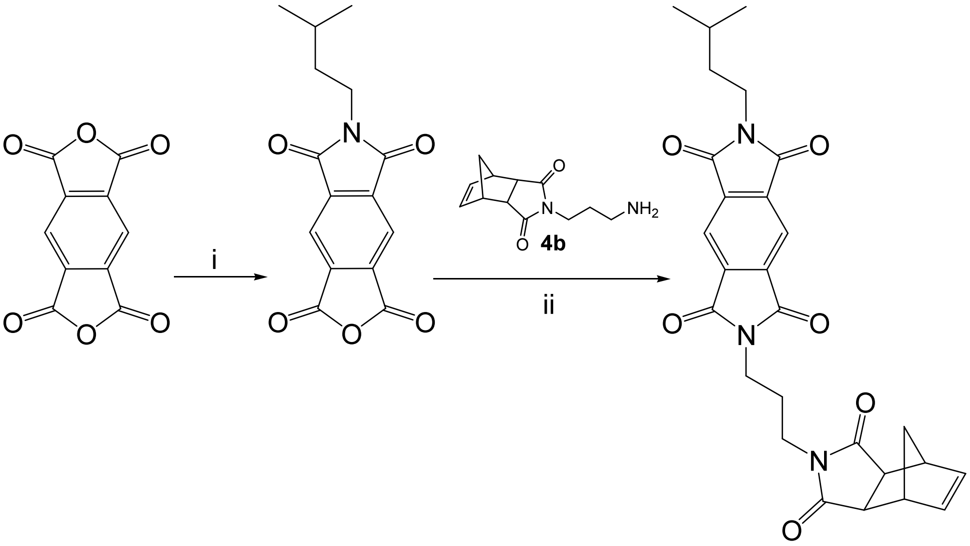
Reagents and conditions: i) $(COCl)_2$, CH_2Cl_2, DMF(< 0.1 mL), 0.5M NH_3 in dioxane; ii) $LiAlH_4$, THF; iii) *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride, DMF, 125 °C, 12h

Compound **3a** and 3**b** was synthesized according to the reported procedures.[6]

Monomer **3** was synthesized using the same procedure as that for the monomer **1**. The product was purified using silica as then packing material and mixture of hexane and DCM (1:9) as the eluent to yield the monomer **3** as a pale yellow powder in 70% yield.

Mp: 131 °C; IR ν_{max}: 661, 712, 773, 821, 851, 897, 1019, 1101, 1143, 1154, 1223, 1287, 1322, 1337, 1390, 1430, 1457, 1695, 1767, 2942 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):δ 1.22 (1H, d, J = 9.5 Hz), 1.48 (1H, d, J = 9.5 Hz), 1.78 (2H, m), 1.88 (2H, m), 2.66 (2H, s), 3.27 (2H, s), 3.38 (2H, t, J = 7.5 Hz), 3.57 (2H, t, J = 7.5 Hz), 6.28 (2H, s), 7.86-8.17 (9H, m); ^{13}C NMR (100.57 MHz, $CDCl_3$): δ 28.24, 29.50, 33.38, 38.85, 43.11, 45.55, 48.19, 123.72, 125.117, 125.25, 125.42, 125.48, 126.20, 127.03, 127.68, 127.91, 128.98, 130.27, 131.30, 131.82, 136.61, 138.18, 178.5; MS (HRMS) calcd for $C_{29}H_{25}NO_2$ (M^+) (419.1885); found 419.1878.

Synthesis and characterization of **4**



4a **4**

Scheme: 4

Reagents and conditions: i) isoamylamine, DMF (dry), 80 °C, 12 h; ii) DMF (dry), 120 °C, 12 h

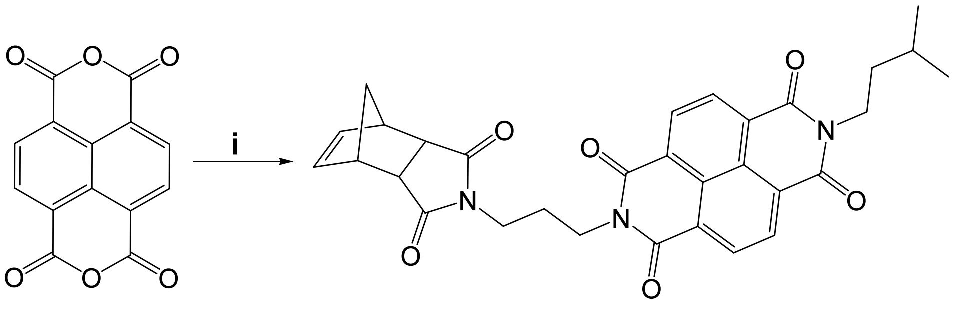
6-isopentyl-6H-furo[3,4-f]isoindole-1,3,5,7-tetraone (4a) Compound **4a** was synthesized according to the reported procedure.[7] Compound **4a** was purified by column chromatography (silica as the packing material and mixture of DCM and ethyl acetate (3:2) as the eluent). The pure product is higly sensitive to the moisture and thus characterised by mass spectroscopy. MS (FAB) calcd for $C_{15}H_{13}NO_5$ ($M+H^+$). (288.08); found 288.

Compound **4b** A suspension of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (1.5 g, 9.13 mmol) in 15 mL of DMF was heated to 100 °C, after which 1,3-diaminopropane (3.82 mL, 45.68 mmol) was added quickly in argon atmosphere. The resulting mixture was heated at 125 °C for 12 h. The reaction mixture was poured into 250 mL of cold water and extracted using dichloromethane. The crude mixture contains disubsituted imide was removed by column chromatography using silica as the packing material and DCM:methanol (9:1) mixture as the eluent. The compound **4b** was then eluted out using methanol can be directly used for next step after evaporating off the solvent.

Monomer **4** was synthesised using the same procedure as that for the monomer **1**. The product was purified using silica as then packing material and mixture of hexane and DCM (1:9) as the eluent to yield the monomer **4** in 58% yield.

white powder; Mp: 187 °C IR ν_{max}: 665, 726, 785, 817, 867, 954, 996, 1055, 1080, 1146, 1156, 1204, 1276, 1329, 1341, 1371, 1396, 1449, 1695, 1769, 2956 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 0.99 (6H, d, J = 5 Hz, CH$_3$), 1.28 (1H, m), 1.62 (4H, m), 2.03 (2H, m), 2.71 (2H, s), 3.28 (2H, s), 3.56 (2H, t, J = 6.5 Hz), 3.77 (4H, m), 6.30 (2H, s), 8.27 (2H, s); ^{13}C NMR (100.57 MHz, CDCl$_3$): δ 22.70, 26.31, 27.13, 36.36, 36.62, 37.50, 37.58, 43.19, 45.57, 48.24, 118.57, 137.46, 137.76, 138.22, 166.54, 166.59, 178.35; MS (HRMS) calcd for $C_{27}H_{27}N_3O_6$ (M$^+$). (489.1900); found 489.1905.

Synthesis and characterization of **5**



5

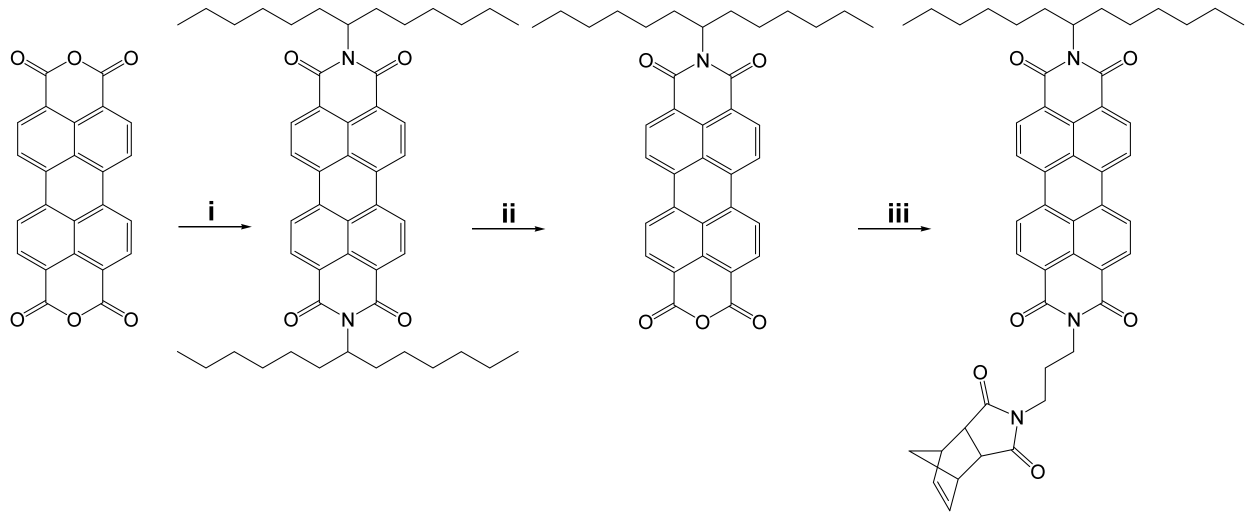
Scheme: 5

Reagents and conditions: i) **4b**, isoamylamine, Imidazole, Zinc acetate, DMF, 130 °C, 12h

Monomer **5**: In a modification of a previous report by Würthner *et* al[8], 1,4,5,8-Naphthalene-tetracarboxylic dianhydride (913.75 mg, 3.4 mmol) was reacted with a mixture of compound **4b** (750 mg, 3.4 mmol), Isoamylamine (0.39 mL, 3.4 mmol), Imidazole (696 mg, 10.22 mmol) and Zinc acetate (625.08 mg, 3.4 mmol) in 5 mL of DMF at 130 °C for 12 h. After cooling to room temperature, the reaction mixture poured in to 50 mL of cold water and neutralized with 5% HCl. The resulting mixture was extracted with dichloromethane and the crude mixture obtained was purified by column chromatography (silica as the packing material and mixture of DCM and ethyl acetate (7:3) as the eluent).

Pale yellow powder; 40 %; Mp: 224 °C; IR ν_{max}: 661, 720, 771, 787, 897, 1000, 1023, 1059, 1087, 1146, 1167, 1200, 1244, 1331, 1373, 1453, 1581, 1661, 1699, 2963 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 1.03 (6H, d, J = 6.5 Hz), 1.38 (1H, d, J = 9.5 Hz), 1.63 (4H, m), 2.06 (2H, m), 2.73 (2H, s), 3.3 (2H, s), 3.64 (2H, t, J = 7 Hz), 4.22 (4H, m), 6.30 (2H, s), 8.74 (4H, m); ^{13}C NMR (100.57 MHz, CDCl$_3$): δ 22.89, 26.83, 27.07, 36.83, 37.2, 38.93, 39.96, 43.22, 45.6, 48.28, 126.78, 127.06, 127.17, 131.27, 131.42, 138.26, 163.11, 163.17, 178.46; MS (HRMS) calcd for $C_{31}H_{29}N_3O_6$ (M$^+$). (539.2056); found 539.2037.

Synthesis and characterization of **<u>6</u>**



6a **6b** **6**

Scheme: 6

Reagents and conditions: i) 1-hexylheptylamine[9], imidazole, 180 °C, 5h; ii) *t*-BuOH, KOH (85%), 90 °C, 1.5h; iii) **4b**, Imidazole, 160 °C, 4h

Compounds **6a**, **6b** and **6** were synthesised according to the reported procedures.[10-12] The crude product **6** obtained was finally purified by column chromatography (silica as the packing material and mixture of DCM and ethyl acetate (7:3) as the eluent. Dark red powder; 65 %; Mp: 265 °C; IR ν_{max}: 690, 718, 747, 811, 861, 958, 1099, 1112, 1141, 1179, 1213, 1249, 1341, 1402, 1438, 1594, 1647, 1689, 2862, 2927 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 0.84 (6H, t), 1.24-1.40 (18H, m), 1.89 (2H, m), 2.08 (2H, m), 2.26 (2H, m), 2.74 (2H, s), 3.31 (2H, s), 3.67 (2H, t), 4.24 (2H, t), 5.19 (1H, m), 6.31 (2H, s), 8.58 (8H, m); ^{13}C NMR (100.57 MHz, CDCl$_3$): 14.46, 23.00, 27.11, 27.38, 29.64, 32.18, 32.76, 37.05, 38.60, 43.26, 45.62, 48.30, 55.23, 123.13, 123.17, 123.35, 126.43, 126.52, 129.51, 129.72, 131.57, 134.36, 134.86, 138.27, 163.49, 178.51; MS (HRMS) calcd for $C_{49}H_{49}N_3O_6$ (M$^+$) 775.3621; found 775.3634.

General procedure for the synthesis of homopolymers[13]

A known amount of monomer was weighed into a Schlenk flask, degassed three times by freeze- pump-thaw cycles, and dissolved in known volume of anhydrous CH_2Cl_2. Into another vial, a desired amount of third generation Grubbs' catalyst was added, flushed with argon, and dissolved in known volume of anhydrous CH_2Cl_2. A known volume of catalyst in CH_2Cl_2 was transferred to the flask containing monomer via syringe. The reaction was allowed to stir at room temperature until the polymerization is complete (2 h), after which ethyl vinyl ether (0.2 mL) was added to quench the polymerization. The product is precipitated from appropriate solvents (MeOH or hexane), collected by suction filtration, dissolved and precipitated a second time.

General procedure for random copolymer synthesis[13]

A known amount of monomers (A and B) were weighed into a Schlenk flask, degassed three times by freeze-pump-thaw cycles, and dissolved in known volume of anhydrous CH_2Cl_2. Into another vial, a desired amount of third generation Grubbs' catalyst was added, flushed with argon, and dissolved in known volume of anhydrous CH_2Cl_2. A known volume of catalyst in CH_2Cl_2 was transferred to the flask containing monomer via syringe. The reaction was allowed to stir at room temperature until the polymerization is complete (2 h), after which ethyl vinyl ether (0.2 mL) was added to quench the polymerization. The product is precipitated from appropriate solvents and purified.

Physical data for P1-15:

P1a A 50mer was prepared by reacting monomer **1** (74 mg, 0.2 mmol) and third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 723, 750, 968, 1119, 1166, 1222, 1333, 1396, 1454, 1484, 1597, 1697, 1771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):δ 1.5 (4H, s), 1.75-2.25 (3H, br), 2.35-2.7 (1H, br), 2.7-3.4 (4.28H, br), 3.4-3.7 (0.8H, br), 3.8-4.15 (1.26H, br), 4.15-4.4 (0.74H, br), 5.35-5.7 (2H, br), 7.0-7.5 (6.9H, br), 7.85-8.1 (1.9H, br); ^{13}C NMR (125.74 MHz, $CDCl_3$): δ 26.91, 36.42, 40.62, 40.89, 41.30, 42.42, 42.85, 45.76, 46.25, 50.82, 51.73, 52.50, 52.95, 122.85, 122.95, 125.71, 126.46, 131.71, 132. 65, 133.53, 140.0, 177.91

P1b A 10mer was prepared by reacting monomer **1** (74 mg, 0.2 mmol) and third generation Grubb's catalyst (0.02 mmol).

IR ν_{max}: 723, 750, 905, 968, 1119, 1154, 1166, 1228, 1326, 1378, 1396, 1452, 1484, 1596, 1693, 1770 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):δ 1.2-2.3 (6.27H, br), 2.35-2.7 (1.14H, br), 2.7-3.7 (5.2H, br), 3.8-4.45 (2.26H, br), 5.35-5.7 (2H, br, d), 7.0-7.5 (6.48H, br), 7.85-8.1 (1.99H, br) ppm; ^{13}C NMR (125.74 MHz, $CDCl_3$): δ 26.78, 36.36, 40.55, 40.84, 41.25, 42.05, 42.37, 45.70, 46.20, 50.67, 51.66, 52.45, 52.86,108.48, 118.99, 120.40, 122.77, 122.88, 125.69, 125.77, 131.69, 132. 61, 133.46, 140.01, 177.95 ppm

P2a A 50mer was prepared by reacting monomer **2** (160 mg, 0.398 mmol) and third generation Grubb's catalyst (0.008 mmol). IR ν_{max}: 750, 903, 971, 1040, 1108, 1129, 1169, 1223, 1255, 1276, 1343, 1396, 1445, 1459, 1697, 1775 cm^{-1};^1H NMR (500 MHz, $CDCl_3$):δ 0.83-0.95 (0.8H, br), 1.21-1.4 (0.74H, s), 1.4-1.7 (3H, br, d), 1.83-2.23 (3.08H, br, t), 2.49-2.78 (1.02H, br d), 2.8-3.13 (2.32H, br), 3.14-3.34 (0.78H, s), 3.34-3.68 (2.02H, br, t), 3.68-3.98 (2.04H, br, t), 5.35-5.77 (2H, br, t), 6.65-7.00 (4.08H, br), 7.00-7.22 (4.02H, br) ppm; ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 25.33, 25.48, 36.58, 40.87, 41.35, 41.46, 41.82, 42.84, 50.83, 50.94, 51.81, 52.31, 52.54, 53.02, 115.33, 115.38, 122.63, 122.71, 124.81, 125.29, 127.32, 127.51, 127.60, 144.90, 144.95, 178.10 ppm

P2b A 10mer was prepared by reacting monomer 2 (80 mg, 0.2 mmol) and third generation Grubb's catalyst (0.02 mmol).

IR ν_{max}: 750, 904, 967, 1038, 1128, 1167, 1260, 1276, 1338, 1394, 1457, 1693, 1770 cm-1; ^{1}H NMR (500 MHz, CDCl$_3$):δ 1.4-1.7 (1.87H, br), 1.83-2.23 (3.12H, br), 2.49-2.78 (1.05H, br, d), 2.8-3.3 (3.09H, br), 3.34-3.68 (2.06H, br, t), 3.68-3.98 (2.06H, br, t), 5.35-5.77 (2H, br), 6.65-7.00 (4.10H, br), 7.00-7.22 (4.07H, br) ppm; ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 25.23, 25.38, 36.50, 40.79, 41.39, 41.72, 42.27, 42.54, 44.70, 45.64, 46.06, 50.72, 50.83, 51.69, 52.19, 52.42, 52.91, 115.33, 115.79, 122.60, 122.68, 124.96, 125.01, 127.30, 127.48, 127.57, 144.83, 144.88, 178.13 ppm

P3a A 50mer was prepared by reacting monomer **3** (41.9 mg, 0.1 mmol) and third generation Grubb's catalyst (0.002 mmol). IR ν_{max}: 722, 752, 842, 907, 966, 1148, 1162, 1263, 1278, 1346, 1396, 1432, 1695, 1773, 2937 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 1.45-2.05 (7.28H, br), 2.05-3.6 (8.36H, br), 5.40-5.62 (1H, s), 5.2-5.65 (2H, s), 7.5-8.3 (9.06H, br) ppm; ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 27.71, 28.84, 28.93, 32.92, 38.14, 38.36, 40.81, 41.49, 42.14, 42.78, 45.74, 46.27, 50.66, 50.90, 51.80, 52.57, 53.02, 123.07, 123.25, 123.33, 124.76, 125.73, 125.80, 126.52, 126.59, 127.15, 127.31, 127.44, 127.54, 128.48, 129.74, 129.85, 130.79, 131.33, 131.68, 133.51, 136.07, 136.25 ppm

P3b A 10mer was prepared by reacting monomer **3** (83.83 mg, 0.2 mmol) and third generation Grubb's catalyst (0.02 mmol). IR ν_{max}: 722, 754, 842, 903, 969, 1148, 1162, 1278, 1343, 1367, 1396, 1438, 1695, 1769, 2937 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 1.48-2.1 (8.06H, br), 2.1-3.6 (8.98H, br), 5.18-5.65 (2H, s), 7.6-8.3(9.52H, br) ppm; ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 27.56, 27.70, 28.82, 32.91, 38.12, 38.34, 40.82, 41.51, 41.95, 42.45, 42.77, 45.72, 45.92, 46.24, 46.91, 50.67, 50.90, 51.81, 52.34, 52.59, 53.00, 123.08, 123.24, 123.32, 124.62, 124.73, 124.84, 124.97, 125.05, 125.71, 125.79, 126.30, 126.51, 126.58, 127.15, 127.30, 127.43, 127.53, 128.27, 128.49, 128.65, 129.74, 129.85, 130.79, 130.85, 131.37, 131.69, 132.72, 133.48, 136.06, 136.24, 138.63 ppm

P4 A 50mer was prepared by reacting monomer **4** (97.8 mg, 0.2 mmol) and third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 727, 760, 823, 856, 974, 1059, 1121, 1139, 1157, 1183, 1364, 1394, 1446, 1706, 1771, 2950 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 0.96 (6.02H, s), 1.50-1.75 (7.41H, br, d), 1.91-2.3 (3.11H, br), 2.65-3.39 (4.06H, br), 3.40-3.60 (2H, br, d), 3.60-3.82 (3.98H, br), 5.5-5.6 (1H, br, d), 5.65-5.85 (0.96H, br, d), 8.15-

8.3 (1.8H, br, d) ppm; ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 22.30, 25.92, 26.49, 36.06, 37.11, 37.17, 41.06, 41.82, 42.14, 42.50, 45.85, 50.89, 51.08, 51.71, 52.28, 52.49, 118.14, 131.85, 131.99, 132.57, 133.37, 137.08, 137.36, 166.13, 166.20, 178.09, 178.28 ppm

P5a A 50mer was prepared by reacting monomer **5** (110 mg, 0.198 mmol) and third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 754, 766, 884, 1087, 1169, 1198, 1244, 1274, 1335, 1379, 1455, 1583, 1661, 1701, 2958 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 1.48-1.8 (5.26H, br), 1.8-2.4(2.99H, br), 2.7-3.2 (3.04H, br), 3.2-3.7(3.04H, br, t), 3.75-4.3 (4.09H, br, t), 5.48-5.53 (1H, s), 5.53-5.58 (1H, br), 8.06-8.56 (4H, br) ppm; ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 22.48, 26.41, 29.71, 36.14, 36.71, 38.04, 39.47, 41.05, 41.97, 45.71, 50.96, 51.17, 51.82, 52.48, 52.94, 126.40, 130.84, 131.86, 133.36, 162.43, 178.42 ppm

P5b A 10mer was prepared by reacting monomer **5** (110 mg, 0.198 mmol) and third generation Grubb's catalyst (0.02 mmol). IR ν_{max}: 754, 766, 882, 973, 1089, 1137, 1169, 1192, 1242, 1278, 1455, 1581, 1659, 1704, 2959 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 0.9-1.04 (6.04H, s), 1.48-1.78 (6.86H, br), 1.8-2.4 (3.11H, br), 2.7-3.2 (3.25H, br, d), 3.2-3.7 (2.97H, br, t), 3.8-4.3 (4.05H, br), 5.4-5.65 (0.95H, s), 5.69-5.90 (1H, br, t), 8.35-8.76 (3.99H, br, d) ppm; ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 22.48, 26.41, 29.70, 36.16, 36.72, 38.04, 39.49, 41.09, 41.98, 42.56, 45.71, 46.01, 46.89, 50.68, 50.98, 51.17, 51.82, 52.44, 52.91, 126.19, 126.34, 126.43, 128.12, 128.50, 128.67, 130.74, 130.85, 131.04, 131.86, 162.46, 162.66, 178.45 ppm

P6 A 50mer was prepared by reacting monomer **6** (76.2 mg, 0.1 mmol) and third generation Grubb's catalyst (0.002 mmol). IR ν_{max}: 747, 811, 851, 1169, 1249, 1333, 1405, 1438, 1579, 1594, 1653, 1693, 2860, 2927 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 0.8-0.98 (8.45H, s), 1.1-1.5 (21.68H, br, d), 1.6-1.7 9 (7.35H, s), 1.7-2.4 (6.43H, br), 2.6-4.18 (6.03H, br), 4.7-5.2 (1H, s), 5.3-5.75 (1.27H, s), 5.75-6.05 (0.28H, s), 7.0-8.4 (7.24H, br); ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 13.09, 21.64, 26.11, 28.23, 28.69, 30.80, 31.27, 35.63, 40.50, 50.23, 51.21, 53.81, 120.96, 123.73, 127.19, 129.20, 131.66, 161.30, 177.65; ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 13.09, 21.64, 26.11, 28.23, 28.69, 30.21, 30.80, 31.27, 35.63, 40.50, 44.59, 50.23, 51.21, 53.81, 120.96, 123.73, 127.19, 129.20, 131.66, 161.30, 177.65

P7 A 50mer random copolymer was prepared by reacting monomer **1** (37mg, 0.1mmol) and monomer **4** (48.95mg, 0.1mmol) in the presence of third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 723, 751, 822, 920, 968, 1057, 1121, 1173, 1276, 1352, 1392, 1449, 1697, 1770, 2940 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$):δ 0.80-1.0 (10.04H, br), 1.2-1.4 (2.56H, br), 1.4-2.3 (21.24H, br), 2.4-3.8 (17.56H, br), 3.8-4.4 (1.6H, br), 5.3-5.8 (4H, br, d), 6.9-7.5 (7.4H, br), 7.5-8.25 (2.64H, br); ^{13}C NMR (125.75 MHz, CDCl$_3$): δ 22.33, 25.94, 26.27, 26.52, 26.92, 35.82, 36.41, 36.68, 37.12, 40.77, 40.88, 41.07, 41.45, 42.11, 42.42, 42.81, 45.79, 46.16, 50.90, 51.81, 52.37, 52.97, 108.20, 108.39, 108.49, 117.59, 117.96, 119.09, 120.36, 122.65, 122.80, 125.78, 126.28, 128.22, 128.53, 131.84, 132.72, 133.33, 136.49, 136.87, 137.16, 139.50, 139.80, 166.05, 177.96, 178.21

P8 A 50mer random copolymer was prepared by reacting monomer **1** (37mg, 0.1mmol) and monomer **5** (55mg, 0.1mmol) in the presence of third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 722, 750, 767, 1085, 1166, 1243, 1332, 1452, 1581, 1660, 1696, 2925 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):δ 0.96-1.05 (7.64H, s), 1.05-1.3 (4.32H, s), 1.35-1.8 (13H, br), 1.8-2.8 (4.48H, br), 2.7-3.7 (10.76H, br), 3.7-4.4 (5.68H, br), 5.31-5.90 (4H, br), 6.80-7.45 (6.88H, br, d), 8.61-8.39 (5.12H, br, t); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 22.50, 26.44, 26.88, 36.23, 36.75, 38.12, 39.45, 40.59, 40.82, 42.08, 42.40, 45.74, 51, 51.86, 52.48, 52.92, 108.39, 118.99, 120.24, 122.67, 125.68, 126.12, 130.25, 130.61, 131.82, 133.44, 139.46, 139.81, 162.43, 178.19

P9 A 50mer random copolymer was prepared by reacting monomer **1** (37mg, 0.1mmol) and monomer **6** (77.6 mg, 0.1mmol) in the presence of third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 722, 748, 809, 850, 1167, 1260, 1335, 1444, 1593, 1653, 1692, 2928 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):δ 0.4-2.3 (172. 92H, br), 2.4-3.7 (24.76H, br), 3.7-4.2 (4.92H, s), 4.3-4.9 (32.52H, s), 4.9-6.0 (4H, br), 6.5-8.5 (56.36H, br); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 14.11, 22.65, 27.06, 27.15, 29.26, 29.69, 31.83, 32.36, 36.43, 37.76, 40.60, 40.78, 41.53, 42.05, 45.72, 50.87, 52.50, 53.44, 54.76, 108.01, 118.98, 120.30, 122.09, 122.77, 123.49, 125.66, 128.52, 130.43, 131.94, 133.29, 139.48, 139.90, 162,47, 177.91

P10 A 50mer random copolymer was prepared by reacting monomer **2** (40.2 mg, 0.1 mmol) and monomer **4** (48.95 mg, 0.1mmol) in the presence of third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 725, 751, 971, 1061, 1121, 1172, 1271, 1354, 1394, 1452, 1696, 1769, 2953 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):δ 0.82-1.04 (6.12H, s), 1.4-1.75 (10.08H, br, d), 1.83-2.3 (6.2H, br, d), 2.4-4.0 (18.16H, br), 5.3-5.8 (4H, br, d), 6.6-7.25 (8.08H, br), 7.95-8.35 (1.8H, br, d); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 22.32, 25.29, 25.45, 25.92, 26.50, 35.87, 36.03, 36.53, 37.12, 41.08, 41.43, 42.07, 44.81, 44.87, 45.77, 50.98, 51.79, 52.50, 53.02, 115.19, 115.31, 118.04, 118.16, 122.59, 122.66, 124.91, 125.32, 126.28, 127.28, 127.45, 127.54, 128.21, 128.52, 131.80, 132.69, 133.38, 136.89, 137.05, 137.20, 137.33, 144.70, 144.85, 166.17, 178.07, 178.19

P11 A 50mer random copolymer was prepared by reacting monomer **2** (40.2 mg, 0.1 mmol) and monomer **5** (55.9 mg, 0.1mmol) in the presence of third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 751, 768, 970, 1086, 1134, 1167, 1244, 1275, 1336, 1374, 1457, 1581, 1664, 1700, 1772, 2950 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$):δ 0.95-1.08 (6.24H, s), 1.42-1.8 (10.24H, br, t), 1.8-2.35 (6.08H, br, t), 2.45-4.3 (18.04H, br), 5.35-5.94 (4H, br), 6.52-7.2 (7.72H, br), 8.40-8.78 (4H, br); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 22.50, 25.22, 25.43, 26.43, 36.54, 36.79, 38.10, 39.51, 41.05, 41.45, 42.27, 44.80, 45.74, 44.80, 45.74, 50.97, 51.82, 52.48, 53.00, 114.97, 115.28, 122.47, 122.63, 124.65, 125.27, 126.21, 126.33, 126.50, 127.27, 127.47, 130.74, 130.85, 131.03, 131.84, 133.36, 144.49, 144.81, 162.51, 162.66, 178.12

P12 A 50mer random copolymer was prepared by reacting monomer **2** (40.2 mg, 0.1 mmol) and monomer **6** (77.6 mg, 0.1mmol) in the presence of third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 747, 809, 850, 964, 1129, 1166, 1248, 1335, 1399, 1447, 1593, 1652, 1692, 1771, 2855, 2923 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$):δ 0.73-0.93 (20.72H, s), 1.1-1.45 (77.48H, br), 1.7-2.4 (16.36H, br), 2.45-4.32 (27.16H, br), 5.1-6.1 (4H, br), 6.5-7.2 (16.4H, br); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 13.10, 21.63, 24.26, 24.42, 26.12, 28.24, 30.80, 31.32, 35.53, 36.95, 39.86, 40.42, 41.36, 43.79, 44.68, 49.91, 51.48, 53.78, 114.26, 121.58, 122.61, 124, 124.24, 125.22, 126.25, 126.43, 127.49, 129.48, 130.71, 132.44, 143.79, 161.53, 177.06

P13 A 50mer random copolymer was prepared by reacting monomer **3** (41.9 mg, 0.1 mmol) and monomer **4** (48.95 mg, 0.1mmol) in the presence of third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 723, 759, 805, 845, 909, 968, 1056, 1144, 1181, 1262, 1358, 1392, 1442, 1697, 1769, 2941 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$):δ 0.85-1.04 (6.72H, s), 1.15-1.32 (4H, s), 1.38-1.85 (17.28H, br), 1.86-2.45 (4.68H, br), 2.5-3.8 (17.72H, br), 5.2-5.9 (4H, br), 7.5-8.3 (9.92H, br); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 21.31, 24.92, 25.58, 26.66, 27.69, 28.69, 31.83, 34.93, 35.84, 36.08, 37.25, 40.04, 40.90, 44.72, 49.90, 50.74, 51.35, 52.00, 115.37, 116.43, 122.28, 123.33, 123.72, 124.82, 125.50, 126.14, 126.32, 127.24, 128.28, 129.91, 130.13, 130.78, 131.76, 132.38, 134.55, 135.39, 164.56, 164.90, 177.20

P14 A 50mer random copolymer was prepared by reacting monomer **3** (27.65 mg, 0.05 mmol) and monomer **5** (20.95 mg, 0.05 mmol) in the presence of third generation Grubb's catalyst (0.002 mmol). IR ν_{max}: 764, 846, 1086, 1163, 1274, 1244, 1336, 1453, 1664, 1699, 2945 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$):δ 0.95-1.15(6.88H, s), 1.45-1.8 (13.96H, br), 1.85-2.5 (4.56H, s), 2.5- 3.78 (13.96H, m), 3.8-4.2 (4.16H, s), 5.3-5.9 (4H, br), 7.3-8.4 (12.48H, br). ^{13}C NMR could not be obtained due to poor solubility/formation of aggregates.

P15 A 50mer random copolymer was prepared by reacting monomer **3** (41.9 mg, 0.1 mmol) and monomer **6** (77.6 mg, 0.1 mmol) in the presence of third generation Grubb's catalyst (0.004 mmol). IR ν_{max}: 746, 808, 844, 1093, 1163, 1253, 1398, 1437, 1578, 1593, 1652, 1692, 1771, 2855, 2923 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$):δ 0.75-0.95 (8.64H, s), 1.1-1.7 (37.84H, br), 1.98-2.4 (4.6H, br, d), 2.42-4.2 (7.84H, br), 4.6-5.8 (4H, br), 6.1-8.15 (16.52H, br); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 13.13, 21.65, 26.14, 27.61, 28.27, 28.67, 30.84, 31.36, 36.97, 40.76, 44.70, 49.93, 51.57, 52.45, 53.65, 120.58, 121.82, 123.45, 124.52, 125.35, 125.83, 127.18, 128.95, 130.69, 131.63, 134.86, 161.42, 177.23

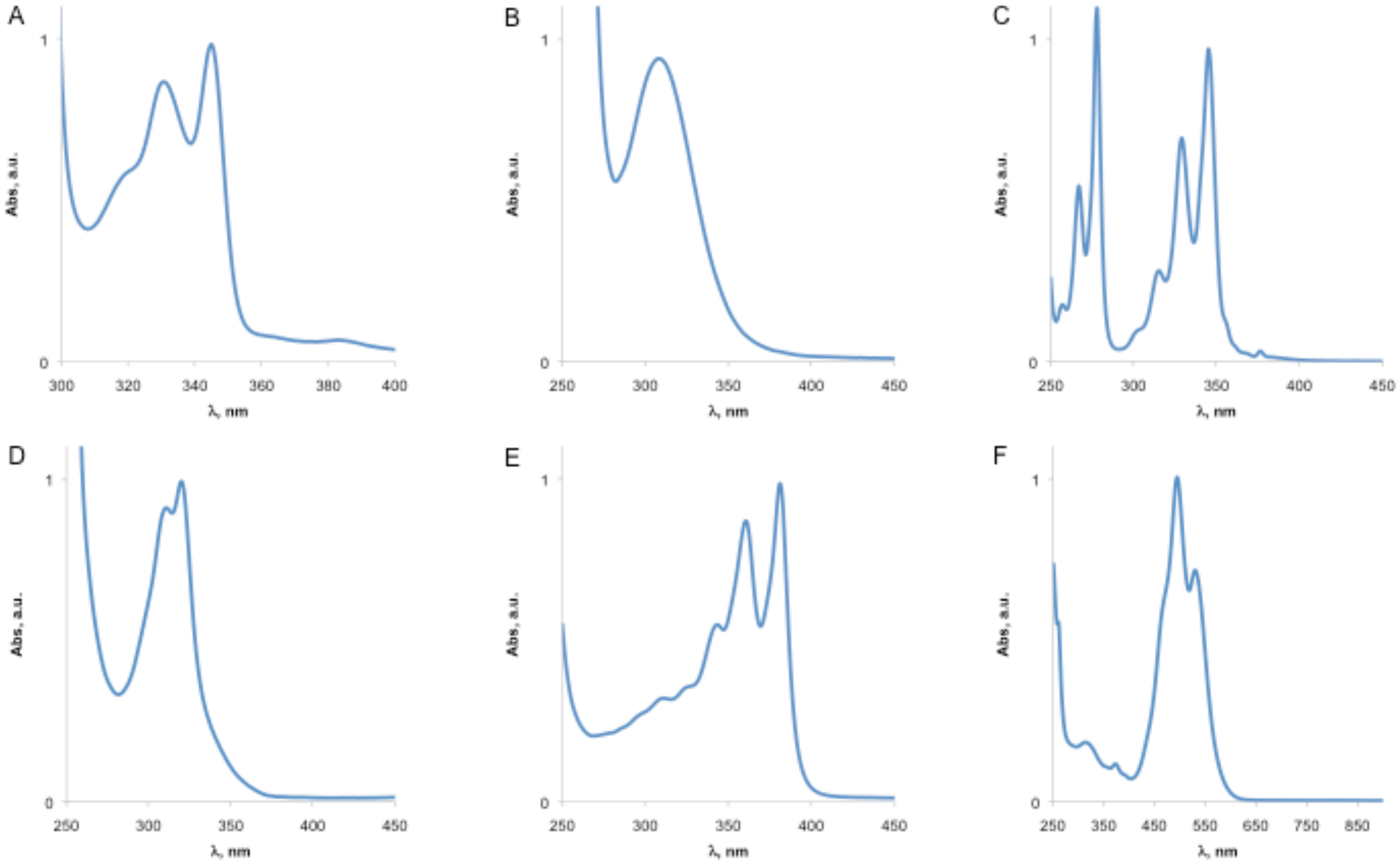


Figure S1. Absorption spectra of homopolymers **P1** (A), **P2** (B), **P3** (C), **P4** (D), **P5** (E), **P6** (F).

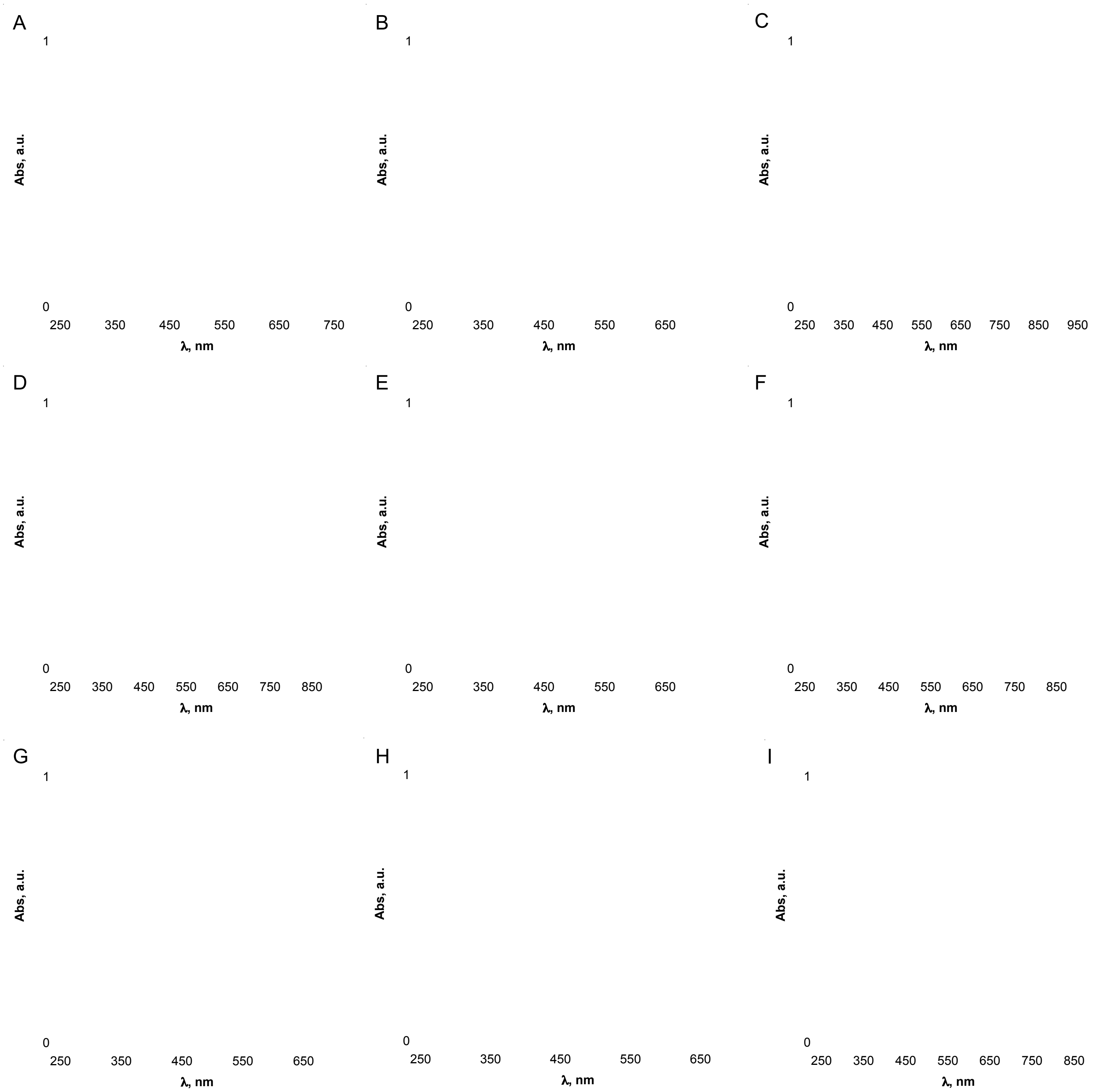


Figure S2. Absorption spectra of copolymers **P7** (A), **P8** (B), **P9** (C), **P10** (D), **P11** (E), **P12** (F), **P13** (G), **P14** (H), **P15** (I).

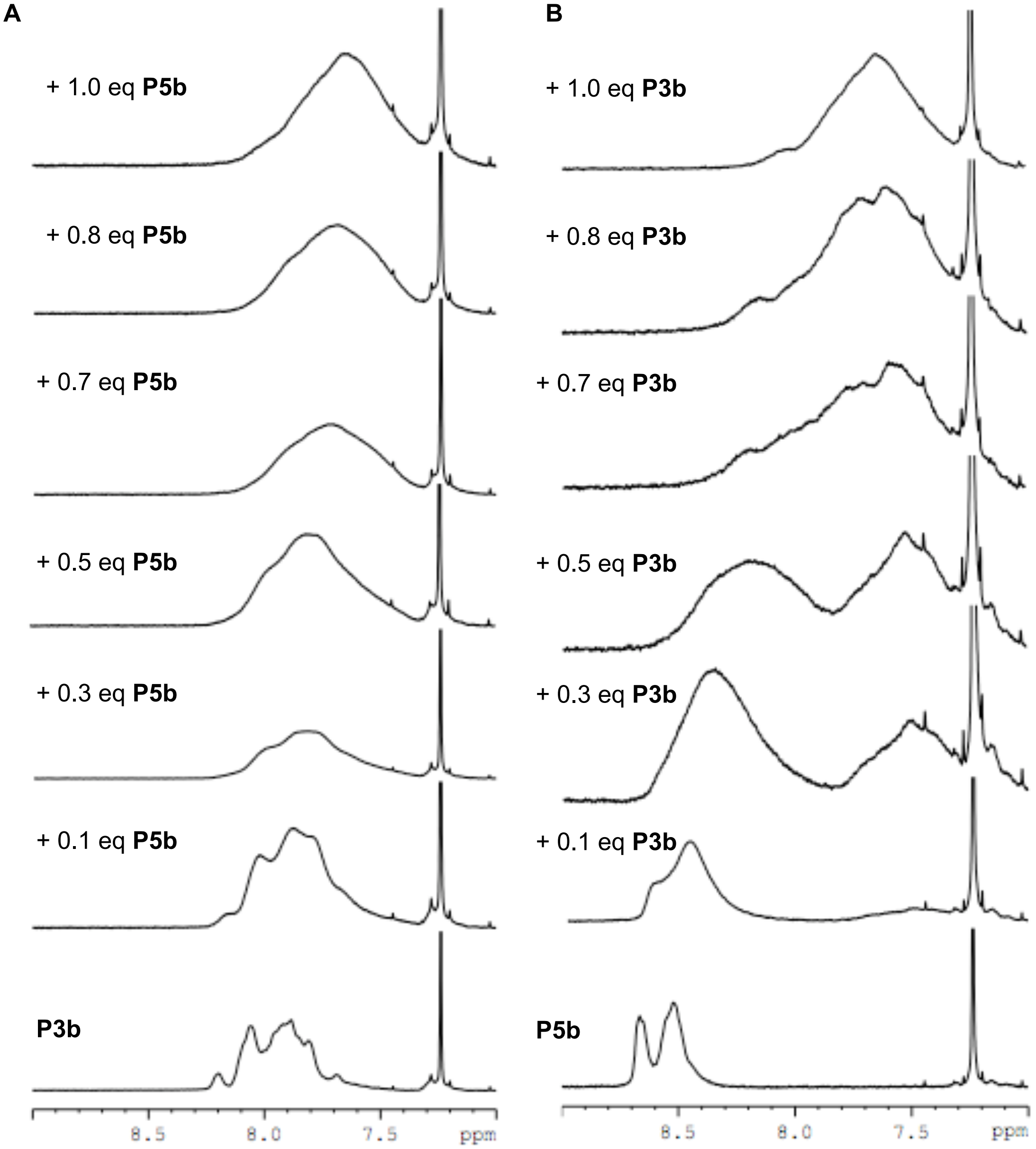


Figure S3. ^{1}H-NMR titrations of **P5b** added to **P3b** (A, at left) and **P3b** added to **P5b** (B, at right).

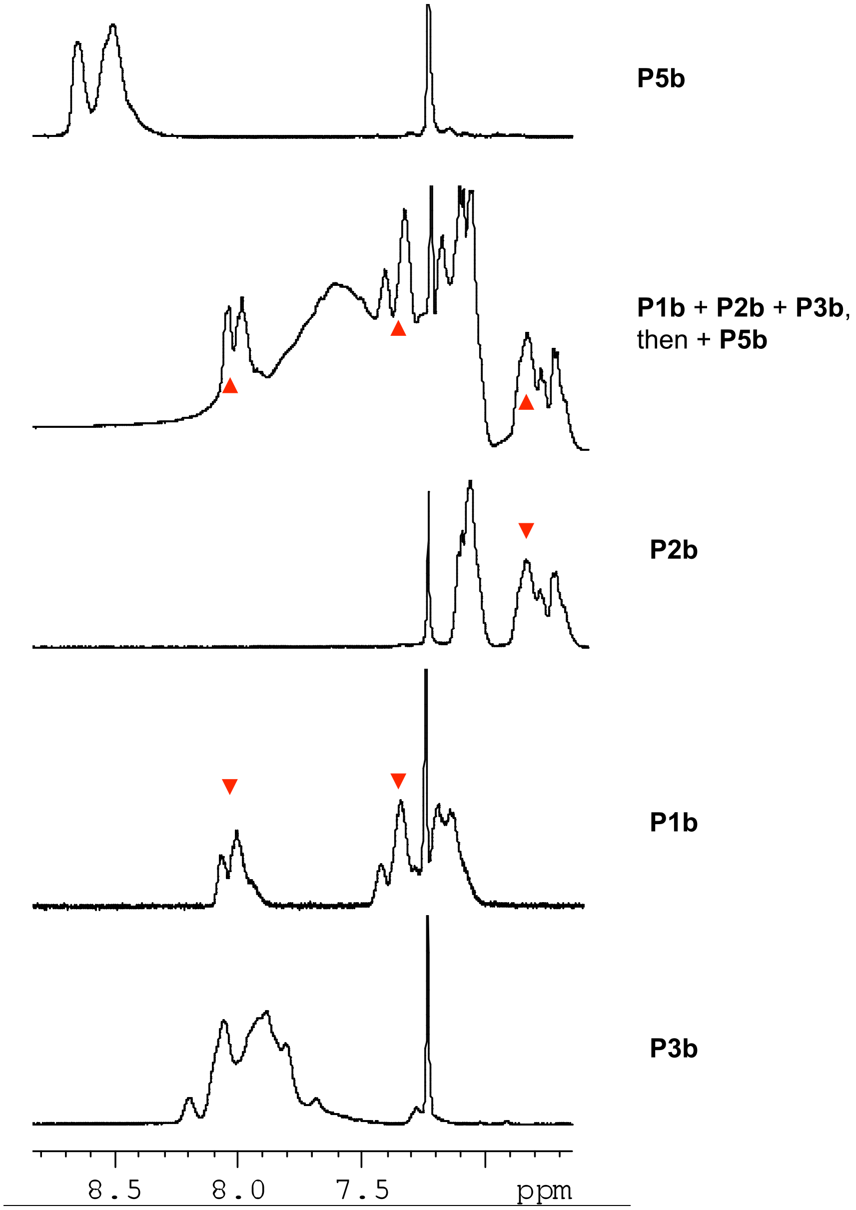


Figure S4. ^{1}H-NMR of NDI containing polymer **P5b** (top) and the π-electron donor containing oligomers (*n* = 12), **P1b**, **P2b** and **P3b** (bottom). When **P5b** is added to a 1:1:1 mixture of **P1b**:**P2b**:**P3b**, the pyrene and NDI containing polymers selectively associate yielding a broad peak centered at 7.6 ppm. The peaks corresponding to the aromatic protons of **P1b** and **P2b** (phenothiazine and carbazole containing polymers) are virtually unchanged (red arrows).

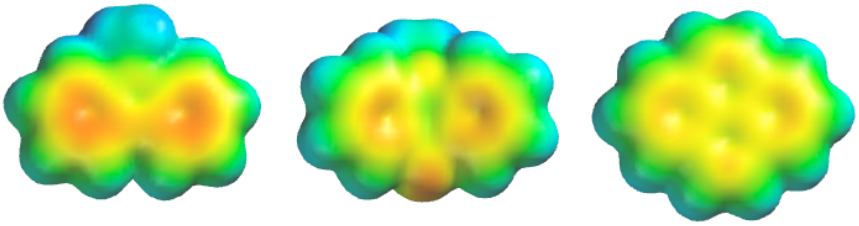


Figure S5. Electrostatic potential map of N-methyl carbazole (left), N-methyl phenothiazine (middle) and pyrene (right).

Table S1. Summary of chromophore oxidation and reduction potentials and Rehm-Weller analysis of PET.

Compound	E_{ox} (V)[a]	E_{red} (V)[a]	E_{00} (V)[21]	ΔG_{PET} (V)[19-21]
carbazole	1.32[14]	-	3.48	-
phenothiazine	0.61[15]	-	2.72	-
pyrene	1.60[16]	-	3.29	-
PMI	-	-0.89[17]	3.54	-
NDI	-	-0.45[18]	3.18	-
PDI	-	-0.58[18]	2.32	-
P7 [b]	1.32	-0.89	3.48 [b]	-1.27
P7 [c]	1.32	-0.89	3.54 [c]	-1.33
P8 [b]	1.32	-0.45	3.48 [b]	-1.71
P8 [c]	1.32	-0.45	3.18 [c]	-1.41
P9 [b]	1.32	-0.58	3.48 [b]	-1.58
P9 [c]	1.32	-0.58	2.32 [c]	-0.42
P10 [b]	0.61	-0.89	2.72 [b]	-1.22
P10 [c]	0.61	-0.89	3.54 [c]	-2.04
P11 [b]	0.61	-0.45	2.72 [b]	-1.66
P11 [c]	0.61	-0.45	3.18 [c]	-2.12
P12 [b]	0.61	-0.58	2.72 [b]	-1.53
P12 [c]	0.61	-0.58	2.32 [c]	-1.13
P13 [b]	1.60	-0.89	3.29 [b]	-0.8
P13 [c]	1.60	-0.89	3.54 [c]	-1.05
P14 [b]	1.60	-0.45	3.29 [b]	-1.24
P14 [c]	1.60	-0.45	3.18 [c]	-1.13
P15 [b]	1.60	-0.58	3.29 [b]	-1.11
P15 [c]	1.60	-0.58	2.32 [c]	-0.14

[a] Redox potentials are presented relative to SHE and are based on the model compounds in the provided references.

[b] Calculated with respect to donor emission

[c] Calculated with respect to acceptor emission

References

1. I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, *2nd Ed.*, Academic Press, New York, **1971**.
2. B. Valeur, *Molecular Fluorescence*, Wiley-VCH, Weinheim, **2002**.
3. Z. Wang, K. Chen, and H. Tian, *Dyes Pigments* **1996**, *30*, 261.
4. E. F. Godefroi, and E. L. Wittle, *J. Org. Chem.* **1956**, *21*, 1163.
5. X. Hu, M. T. Tierney and M. W. Grinstaff, *Bioconjugate Chem*. **2002**, *13*, 83.
6. J. Rebek and T. J. Dale, *J. Am. Chem. Soc*. **2006**, *128*, 4500.
7. R. T. Hayes, C. J. Walsh and M. R. Wasielewski, *J. Phys. Chem. A* **2004,** *108,* 2375.
8. X. Zhang, Z. Chen and F. Würthner, *J. Am. Chem. Soc*. **2007**, *129*, 4886.
9. R. F. Borch, M. D. Bernstein and H. D. Durst, *J. Am. Chem. Soc.* **1971**, *93*, 2897.
10. L. D. Wescott and D. L. Mattern, *J. Org. Chem.* **2003**, *68*, 10058.
11. H. Kaiser, J. Lindner and H. Langhals, *Chem. Ber.* **1991**, *124*, 529.
12. A. Wicklein, A. Lang, M. Muth and M. Thelakkat, *J. Am. Chem. Soc.* **2009**, *131*, 14442.
13. Z. M. AL-Badri and G. N. Tew, *Macromolecules* **2008**, *41*, 4173.
14. F. Loiseau, S. Campagna, A. Hameurlaine and W. Dehaen, *J. Am. Chem. Soc.*, **2005**, *127*, 11352.
15. X. Q. Zhu, Z. Dai, S. Wu and J. P. Cheng, *J. Phys. Chem. B*, **2008**, *112*, 11694.
16. M. Manoharan, K. L. Tivel, M. Zhao, K. Nafisi and T. L. Netzel, *J. Phys. Chem.*, **1995**, *99*, 17461.
17. S. Kato, T. Matsumoto, K. Ideta, T. Shimasaki, K. Goto and T. Shinmozu, *J. Org. Chem.*, **2006**, *71*, 4723.
18. Th. B. Singh, S. Erten, S. Günes, C. Zafer, G. Turkmen, B. Kuban, Y. Teoman, N. S. Sariciftci and S. Icli, *Org. Electron.*, **2006**, *7*, 480.
19. D. Rehm and A. Weller, *Isr. J. Chem.*, **1970**, *8*, 259.
20. J. Kabatc, B. Jedrzejewska and J. Paczkowski, *Polym. Bull.*, **2005**, *54*, 409.
21. H. Y. Hu, M. Z. Zhu, Z. P. Zhang, G. T. Wen and Q. X. Guo, *Chin. J. Chem.,* **200x**, *17*, 333.