Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Solvent-induced emission of organogels based on tris(phenylisoxazolyl)benzene

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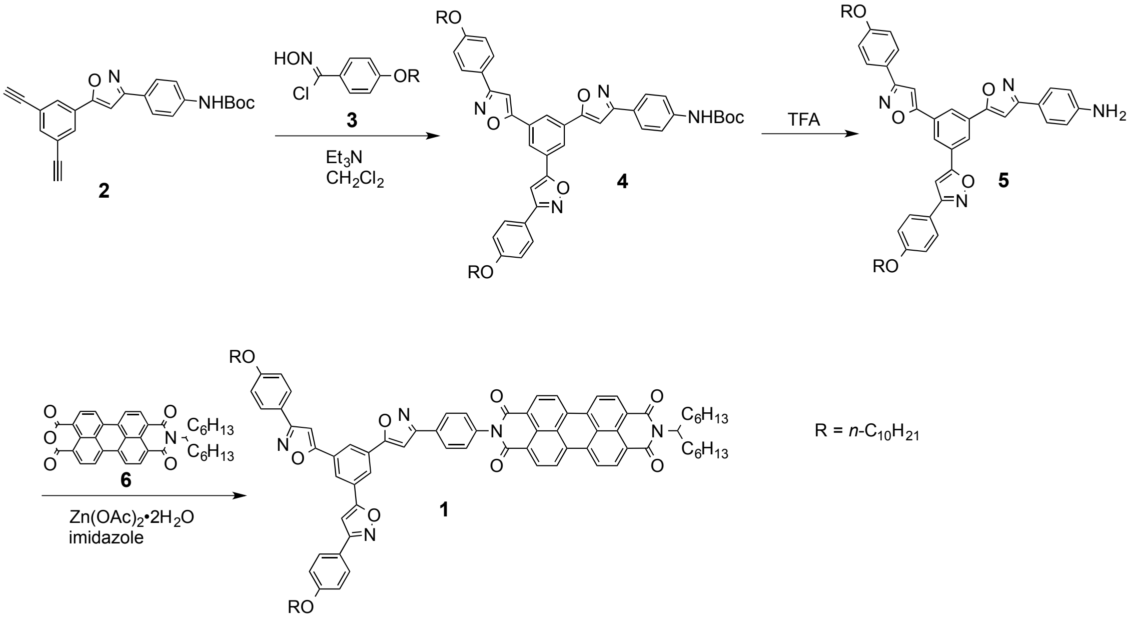
Experimental Section



Scheme S1.

General: All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2, DMF, and triethylamine were obtained by distillation over CaH_2. ^{1}H and ^{13}C NMR spectra were recorded on a Varian mercury-300 spectrometer and JEOL JNM-ECA600 spectrometer at 25 ºC in $CDCl_3$ and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ ($\delta = 7.260$ for ^{1}H and 77.3 for ^{13}C). UV/vis absorption spectra were recorded on a JASCO V-560 spectrometer. Fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorometer. Fluorescence quantum yields were recorded on a JASCO FP-6500 spectrofluorometer with an integrating sphere (JASCO, ILF-533, diameter 10 cm). IR spectra were recorded on JASCO FT/IR-420S spectrometer. ESI-Mass spectra were recorded on Thermo Scientific LTQ Orbitrap XL hybrid FTMS. UV/vis absorption and fluorescence spectra in solution were measured using a conventional quartz cell (light path 1 cm) with temperature control. UV/vis absorption and fluorescence spectra in gel phase were measured using gels drop-casted on quartz plate. Elemental analyses were performed using CHN analyzer. Preparative separations were performed by silica gel gravity column chromatography (Silica Gel 60N (spherical, neutral)). Recycling preparative GPC-HPLC separations were carried out on JAI LC-908s using preparative JAIGEL-2H, 2H, 1H columns in series. Compound **2**,[1] **3**,[1] and **6**[2] were prepared according to the reported methods.

1-{3-[4-(*N-tert*-Butoxycarbonyl)aminophenyl]isoxazol-5-yl}-3,5-bis[3-(4-decyloxyphenyl)isoxazol-5-yl]benzene (4): To a solution of chlorooxime **3** (1.33 g, 4.28 mmol) in CH_2Cl_2 (7 mL) was added **2** (760 mg, 1.98 mmol) and triethylamine (0.80 mL, 5.8 mmol) in CH_2Cl_2 (18 mL). After being stirred at room temperature for 12 h under argon atmosphere, 1N HCl was added to the mixture. After extraction with EtOAc, the organic layer was washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/hexane) to give a desired product (1.11 g, 60%) as a white solid. M.p. 232–234 ºC; ^1H NMR (300 MHz, $CDCl_3$): δ 8.26 (s, 2H), 8.23 (s, 1H), 7.81 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.7 Hz, 4H), 7.49 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 8.7 Hz, 4H), 6.97 (s, 1H), 6.94 (s, 2H), 6.66 (s, 1H), 4.00 (t, J = 6.6 Hz, 4H), 1.81 (m, 4H), 1.60–1.25 (m, 28H), and 0.89 (t, J = 6.3 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 168.0, 162.8, 162.7, 160.8, 152.4, 140.2, 129.3, 129.2, 128.2, 127.6, 123.9, 123.8, 123.1, 120.8, 118.5, 114.9, 98.8, 98.8, 81.0, 68.1, 31.9, 29.6, 29.4, 29.3, 29.2, 28.3, 26.0, 22.7, and 14.1 ppm; IR (KBr): ν 3371, 2927, 1731, 1611, 1529, 1466, 1432, 1389, 1251, 1158, 1051, 951, 792, 656, 534, and 418 cm^{-1}; HRMS (ESI$^+$): calcd for $C_{58}H_{70}N_4O_7Na$ *m/z* 957.5137 $[M+Na]^+$, found *m/z* 957.5101; Anal. calcd for $C_{58}H_{70}N_4O_7•H_2O$: C 73.08, H 7.61, N 5.88, found C 73.01, H 7.53, N 5.99%.

1-[3-(4-Aminophenyl)isoxazol-5-yl]-3,5-bis[3-(4-decyloxyphenyl)isoxazol-5-yl]benzene (5): 4 (792 mg, 0.847 mmol) was dissolved in TFA (8 mL), and the solution was stirred for 1 h at room temperature under argon atmosphere. The reaction was quenched by addition of 10% NaOH aq. in ice bath, and the precipitate was filtered to give a desired product (686 mg, 97%) as a white solid. M.p. 191–193 ºC; ^1H NMR (300 MHz, $CDCl_3$): δ 8.25 (s, 2H), 8.23 (s, 1H), 7.79 (d, J = 8.6 Hz, 4H), 7.67 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.6 Hz, 4H), 6.94 (s, 2H), 6.91 (s, 1H), 6.75 (d, J = 8.7 Hz, 2H), 4.00 (t, J = 6.5 Hz, 4H), 2.90 (br, 2H), 1.81 (m, 4H), 1.59–1.27 (m, 28H), and 0.89 (t, J = 6.3 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 167.6, 163.1, 162.8, 160.9, 148.7, 129.1, 129.0, 128.3, 128.3, 123.6, 123.6 120.9, 118.5, 115.1, 114.9, 98.7, 98.6, 68.3, 32.2, 29.9, 29.9, 29.8, 29.6, 29.5, 26.3, 23.0, and 14.4 ppm; IR (KBr): ν 3390, 2955, 2926, 1615, 1562, 1531, 1468, 1441, 1386, 1295, 1255, 1178, 1017, 951, 835, 794, 762, 651, and 531 cm^{-1}; HRMS (ESI$^+$): calcd for $C_{53}H_{63}N_4O_5$ *m/z* 835.4793 $[M+H]^+$, found *m/z* 835.4788; Anal. calcd for $C_{53}H_{62}N_4O_5•1H_2O$: C 74.62, H 7.56, N 6.57, found C 74.31, H 7.71, N 6.22%.

***N*-{4-{5-{3,5-Bis[3-(4-decyloxyphenyl)isoxazol-5-yl]phenyl}isoxazol-3-yl}phenyl}-*N*'-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (1): 5** (156 mg, 0.187 mmol), perylene monoimide monoanhydride **6** (107 mg, 0.186 mmol), zinc(II)acetate dihydrate (62 mg, 0.28 mmol), and imidazole (1.96 g) were added to a schlenk flask. After being stirred for 3 h at 160 ºC under argon atmosphere, the reaction was quenched by addition of 6N HCl (100 mL). After standing overnight, the precipitate was filtered, and the crude product was further purified by column chromatography on silica gel (EtOAc/hexane) and by GPC. Reprecipitation from chloroform/MeOH gave a desired product (145 mg, 56%) as a dark red solid. M.p. >300 ºC (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.69 (d, J = 7.8 Hz, 2H), 8.66–8.56 (m, 6H), 8.28 (s, 2H), 8.26 (s, 1H), 8.06 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 8.4 Hz, 4H), 7.53 (d, J = 7.8 Hz, 2H), 7.05 (s, 1H), 6.94 (d, J = 8.4 Hz, 4H), 6.93 (s, 2H), 5.11 (m, 1H), 3.95 (t, J = 6.5 Hz, 4H), 2,18 (m, 4H), 1.81 (m, 4H), 1.75 (m, 4H), 1.48 (m, 4H), 1.41 (m, 4H), 1.35–1.12 (m, 32H), 0.81 (d, J = 6.5 Hz, 6H), and 0.76 (d, J = 6.6 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 45 ºC): δ 168.3, 168.2, 168.2, 163.5, 163.1, 163.0, 161.1, 161.1, 137.1, 135.4, 134.3, 132.0, 130.0, 129.8, 129.6, 129.5, 129.4, 128.4, 128.4, 128.1, 126.9, 126.6, 124.2, 124.1, 123.5, 123.3, 123.1, 121.1, 115.2, 115.2, 99.3, 99.0, 68.5, 55.1, 32.6, 32.1, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 27.2, 26.2, 22.8, 22.7, 14.2, and 14.2 ppm; IR (KBr): ν 2928, 2861, 1693, 1662, 1590, 1521, 1441, 1340, 1255, 1172, 1105, 1031, and 818 cm^{-1}; HRMS (ESI$^+$): calcd for $C_{90}H_{96}N_5O_9$ *m/z* 1390.7203 $[M+H]^+$, found *m/z* 1390.7188; Anal. calcd for $C_{90}H_{95}N_5O_9 \bullet 3H_2O$: C 74.82, H 7.05, N 4.85, found C 74.51, H 7.21, N 4.52%.

Analysis of self-association by ^{1}H NMR experiments: Hyperbolic curves were obtained by plotting of compound concentrations vs ^{1}H NMR chemical shifts (δ) of the aromatic protons. The curve-fitting analysis of the plots was carried out on the basis of an isodesmic association model, which is a type of unlimited self-association where the addition of each successive monomer to polymer involves an equal association constant ($K_2 = K_3 = ... = K_i = K_E$). The fitting functions are given by equation 1 for NMR experiments. δ denotes apparent chemical shifts obtained from spectra; δ_m and δ_a are chemical shifts for a monomer and self-assembled species, respectively. K_E is the association constant; and c is the total concentration of a compound. The complexation-induced shift $\Delta\delta$ displays the difference between δ_m and δ_a.

$$\delta(c) = \delta_m + (\delta_a - \delta_m)\left(1 + \frac{1 - \sqrt{4K_E c + 1}}{2K_E c}\right) \qquad (1)$$

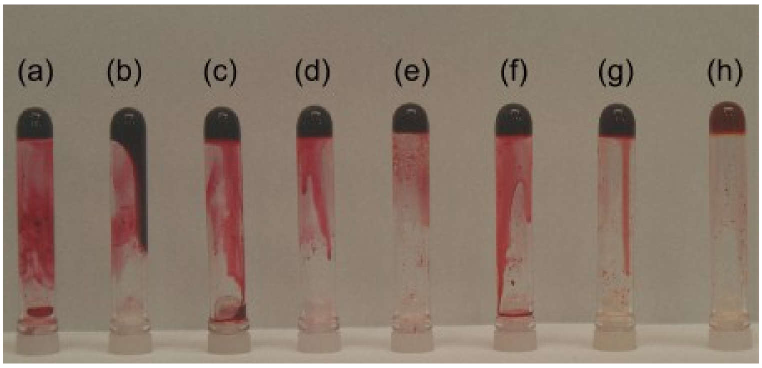


Figure S1. Photograph of the gels of **1**. The solvents are (a) cyclohexane, (b) methylcyclohexane (MCH), (c) benzene, (d) *o*-dichlorobenzene, (e) pyridine, (f) 4-methylpyridine, (g) tetrahydrofurane (THF), and (h) 1,4-dioxane.

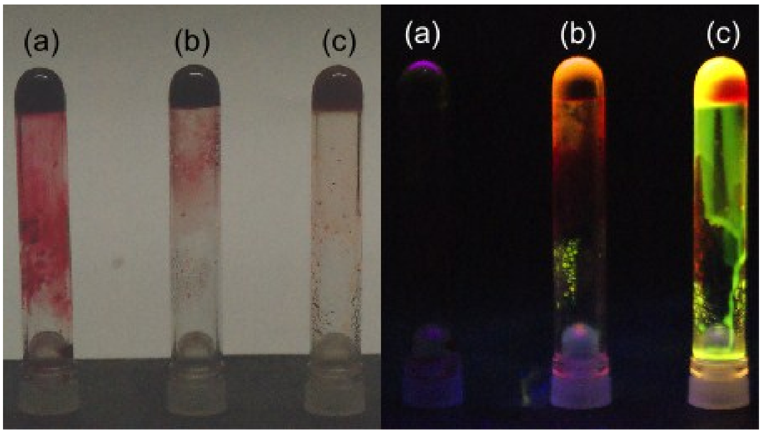


Figure S2. Photograph of the gels of **1** (top) under room light and (bottom) under UV light. The solvents are (a) benzene, (b) pyridine, and (c) 1,4-dioxane.

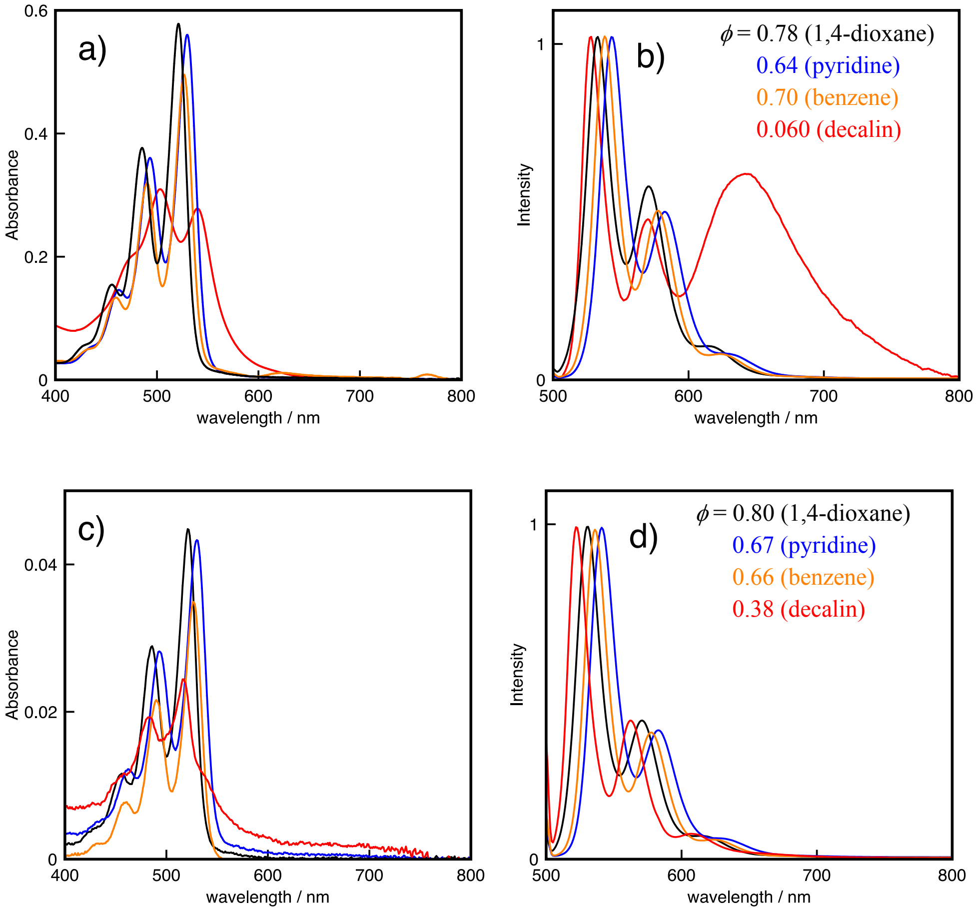


Figure S3. (a, c) UV-vis absorption and (b, d) emission spectra of **1** in (black) 1,4-dioxane, (red) decalin, (blue) pyridine, and (orange) benzene solution at 25 ºC. (a, b) [**1**] = 1.0 × 10^{-5} mol L^{-1} and (c, d) [**1**] = 5.0 × 10^{-7} mol L^{-1}. λ_{ex} = 500 nm.

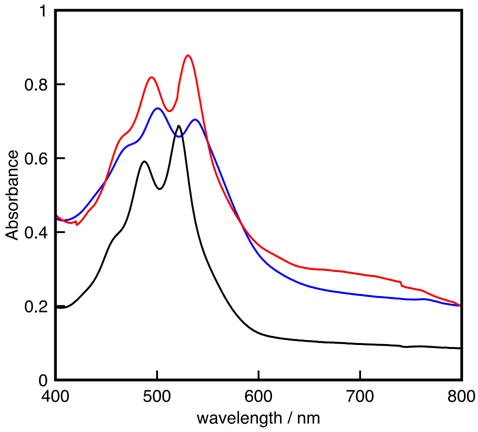


Figure S4. UV-vis absorption spectra of **1** in (black) 1,4-dioxane gel, (red) pyridine gel, and (blue) benzene gel without normalizing the absorbance.

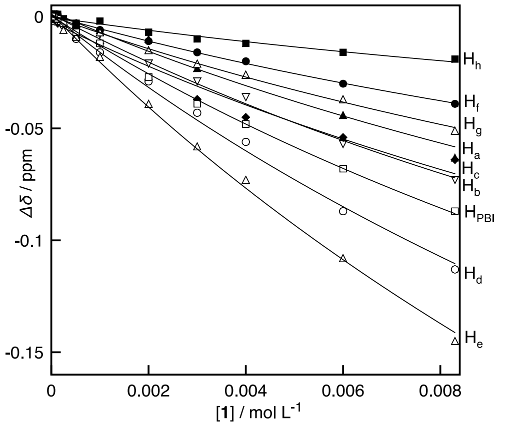


Figure S5. Non-linear curve fitting of **1** using ^{1}H NMR in chloroform-d_1 at 298 K. The lines display fitting curves.

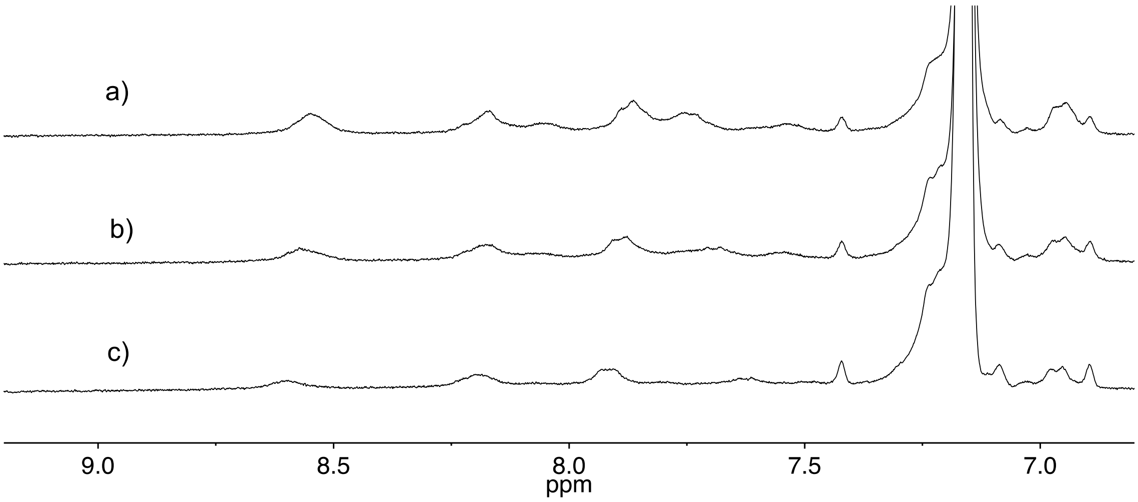


Figure S6. Temperature-dependent ^{1}H NMR spectra of **1** in benzene-d_6. The temperatures are (a) 70 ºC, (b) 50 ºC, and (c) 25 ºC. [**1**] = 3.0 mmol L^{-1}.

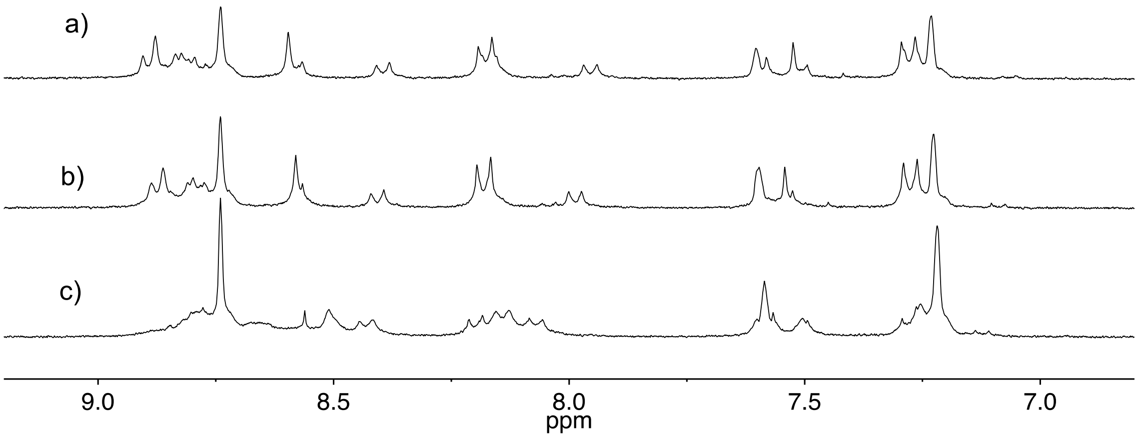


Figure S7. Temperature-dependent ^{1}H NMR spectra of **1** in pyridine-d_5. The temperatures are (a) 70 ºC, (b) 50 ºC, and (c) 25 ºC. [**1**] = 3.0 mmol L^{-1}.

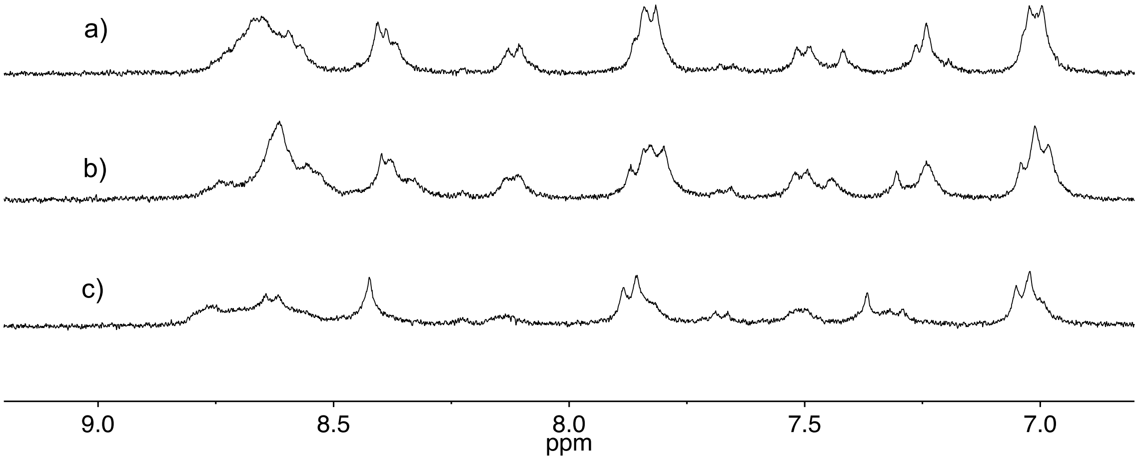


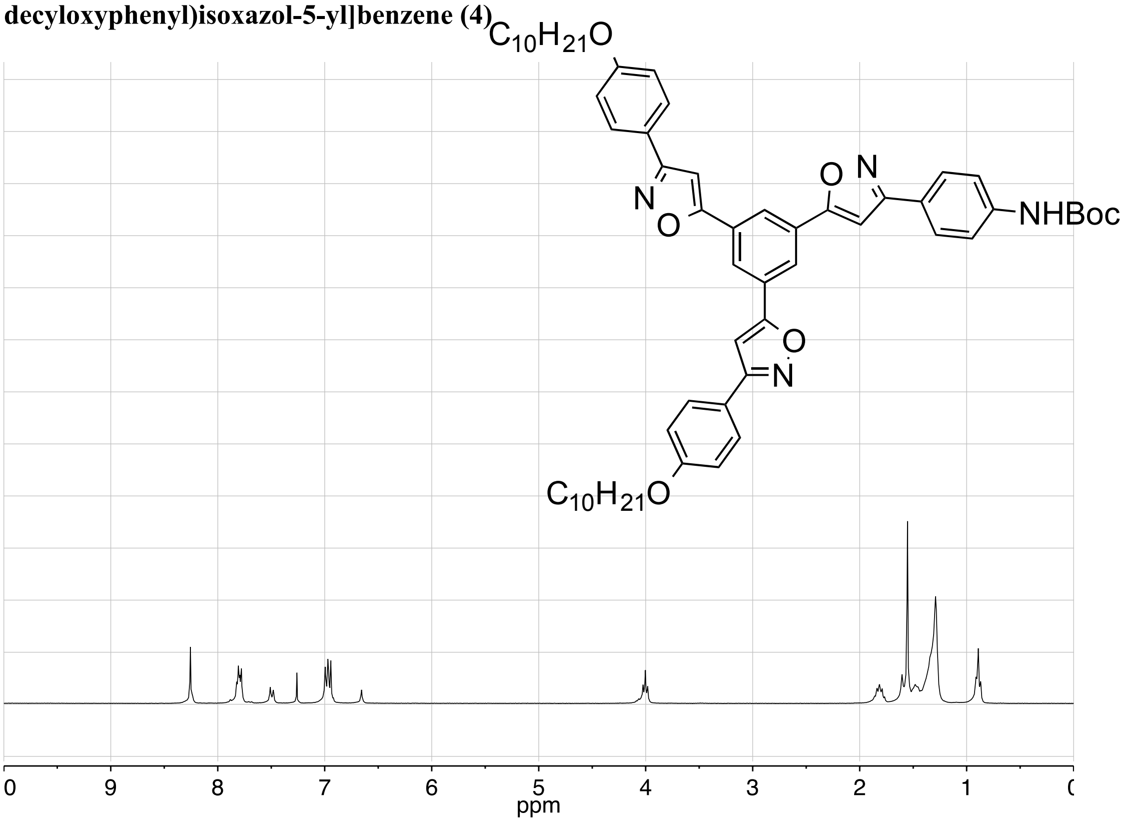
Figure S8. Temperature-dependent ^{1}H NMR spectra of **1** in 1,4-dioxane-d_8. The temperatures are (a) 70 ºC, (b) 50 ºC, and (c) 25 ºC. [**1**] = 3.0 mmol L^{-1}.

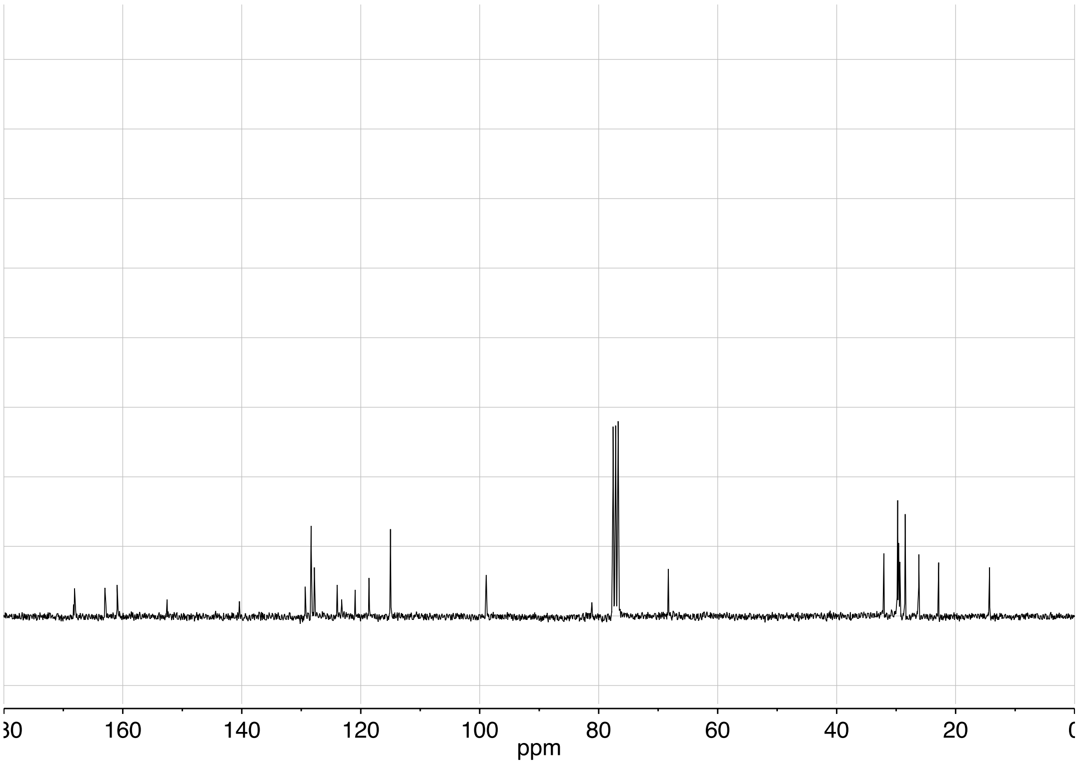
References

1) M. Tanaka, T. Ikeda, J. Mack, N. Kobayashi, T. Haino, *J. Org. Chem.* **2011**, *76*, 5082–5091.

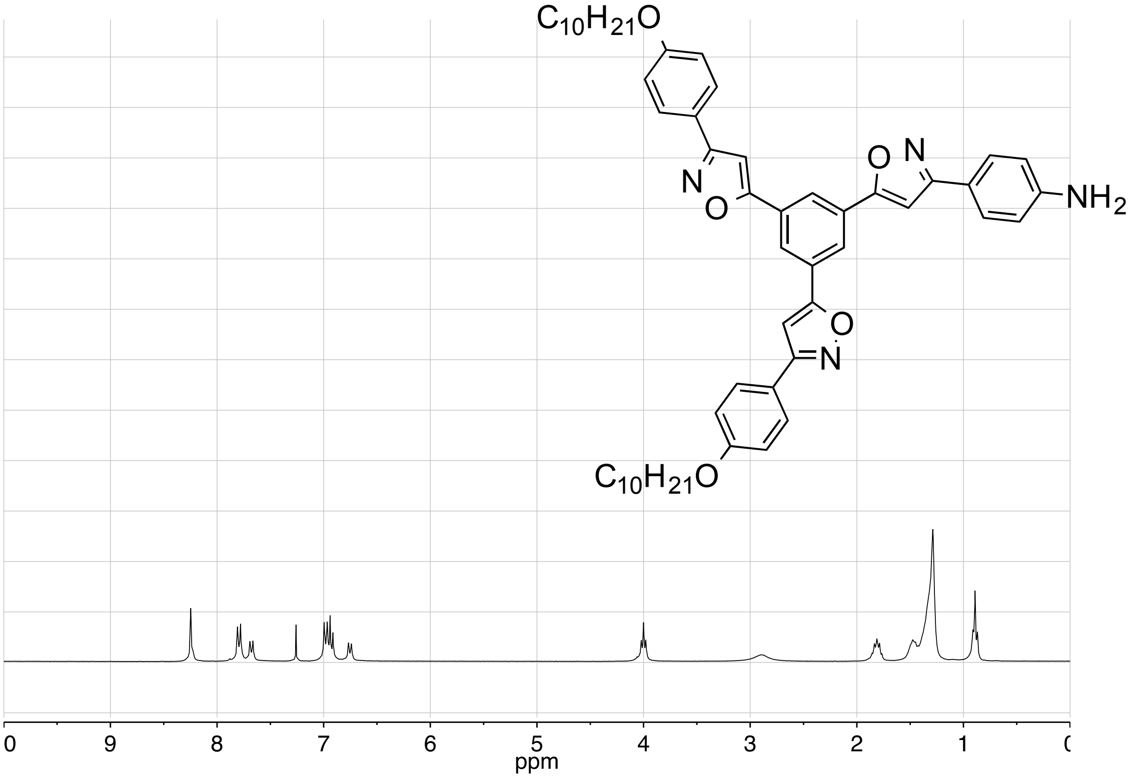
2) T. Ikeda, T. Masuda, T. Hirao, J. Yuasa, H. Tsumatori, T. Kawai, T. Haino, *Chem. Commun.* **2012**, *48*, 6025–6027.

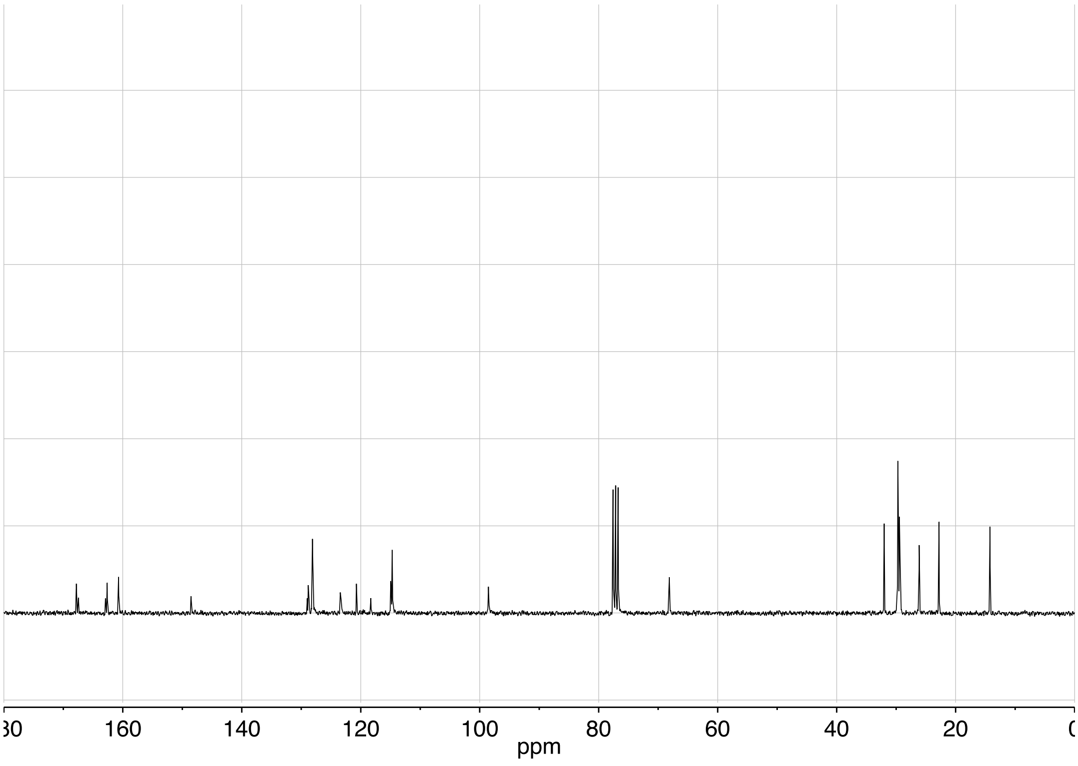
1-{3-[4-(*N*-*tert*-Butoxycarbonyl)aminophenyl]isoxazol-5-yl}-3,5-bis[3-(4-decyloxyphenyl)isoxazol-5-yl]benzene (4)





1-[3-(4-Aminophenyl)isoxazol-5-yl]-3,5-bis[3-(4-decyloxyphenyl)isoxazol-5-yl]benzene (5)





***N*-{4-{5-{3,5-Bis[3-(4-decyloxyphenyl)isoxazol-5-yl]phenyl}isoxazol-3-yl}phenyl}-*N'*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (1)**