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Supporting Information

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Amplified and Differentiated Binding in a 1-D Organogel Matrix Leads to a Spontaneous Colorimetric Sensing of Positional Isomers of Dihydroxynaphthalenes

by

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Experimental section

Techniques:

^{1}H NMR spectra were measured on a Bruker DMX 600 spectrometer. IR spectra were obtained using a Perkin Elmer ATR FTIR spectrometer. UV/Vis spectra were measured on a Shimadzu UV-2500PC spectrophotometer. Mass spectral data were obtained using a Perseptive Biosystems Voyager-DE STR MALDI TOF mass spectrometer.

SEM measurements: The samples were prepared by freezing and pumping the cyclohexane gels of **1** and **1・3f** for 12 h. The xerogel of **1** and **1・3f** thus obtained were shielded by Pt (30 s) and examined with a Hitachi S-5500 scanning electron microscope.

TEM measurements: These measurements were performed at 120 kv using JEOL 2010. The cyclohexane gel of **1** was cast on a carbon-coated copper grid, and dried at room temperature. Measurements were performed without staining the sample.

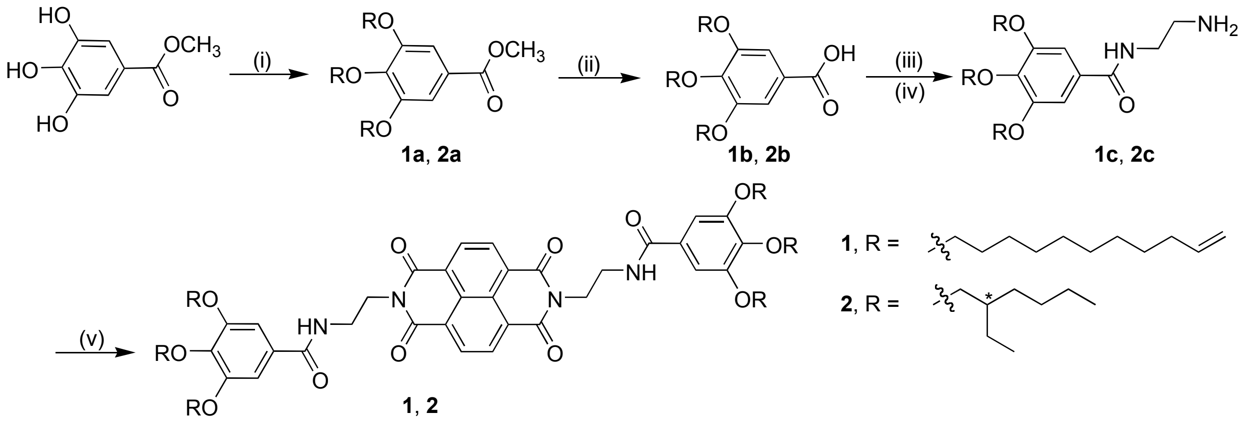
Molecular Modeling: Modeling studies of **1** and **1・3f** complex was performed using the Discover 3/Insight II 98.0 software.

Materials:

All chemicals and solvents were purchased from Aldrich or Tokyo kasei Chemicals, and were used as received.

Synthesis of compounds 1 and 2:

Scheme S1.



Reagents and Conditions: (i) 11-bromo-1-undecene or 2-ethylhexylbromide, K_2CO_3, DMF, 60 °C, 20 h; (ii) NaOH, THF/water, 70 °C, 4 days; (iii) $SOCl_2$, RT, 30 min; (iv) ethylene diamine, 0 °C-RT, 10 h; (v) 1,4,5,8-naphthalenetetracarboxylic dianhydride, DMF, 140 °C, 6 h

Synthetic procedures

1a: In a 300 mL round-bottomed flask 3,4,5-trihydroxyphenyl methylester (0.50 g, 2.72 mmol), anhydrous K_2CO_3 (3.37 g, 24.4 mmol) was taken and dissolved in 50 mL of dry DMF. The mixture was heated and stirred at 60 °C for 1.5 h. Subsequently 11-bromo-1-undecene (3.81 g, 16.3 mmol) was added and the mixture was stirred for 20 h at 60 °C. The mixture was poured in 100 mL of water and extracted with EtOAc. The organic layer was washed with brine solution (5 x 50 mL), dried over anhydrous $MgSO_4$ and the solution was evaporated using a rotary evaporator. The crude product obtained was purified by column chromatography [silica gel, hexane/chloroform 7:3] to obtain **1a** as colorless oil (1.53 g, 88%); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.21\text{-}1.62$ (m, 36H; CH_2), 1.79-1.82 (m, 6H; $OCH_2C\mathit{H}_2$), 2.02 (q, ^3J (H, H) = 7.1 Hz, 6H; $=CHC\mathit{H}_2$), 3.89 (s, 3H; $COOCH_3$), 4.01 (t, ^3J (H, H) = 6.4 Hz, 6H; OCH_2), 4.92-5.00 (m, 6H; $=CH_2$), 5.79-5.83 (m, 3H; $=C\mathit{H}CH_2$), 7.25 (s, 2H; ArH); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 26.47$, 28.91, 28.98, 29.36, 29.49, 29.56, 29.61, 29.71, 29.78, 29.87, 29.95, 29.97, 30.07, 30.65, 30.73, 34.23, 52.96, 69.53, 73.86, 108.31, 114.43, 114.58, 125.07, 139.34, 139.82, 142.73, 153.22, 167.34; MS (MALDI-TOF, matrix; dithranol): 663.97 calcd $[M + Na]^+$, found 663.60 $[M + Na]^+$.

2a: The same procedure as above was followed using 2-ethylhexylbromide. The crude product obtained was purified by column chromatography [silica gel, hexane/chloroform 6:4] to obtain **2a** as colorless oil (1.3 g, 93%); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.91\text{-}0.97$ (m, 18H; CH_3), 1.34-1.36 (m, 12H; CH_2), 1.42-1.57 [m, 13H; CH_2 (12) and $OCH_2C\mathit{H}$ (1)], 1.77-1.78 (m, 2H; $OCH_2C\mathit{H}$), 3.89-3.96 (m, 9H; OCH_2 and $COOCH_3$), 7.29 (s, 2H; ArH); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 11.59, 14.50, 14.54, 23.34, 23.49, 23.54, 24.07, 24.24, 29.52, 29.70, 30.85, 30.93, 39.99, 41.04, 52.49, 71.63, 76.31, 107.78, 124.92, 142.66, 153.42, 167.44; MS (MALDI-TOF, matrix; dithranol): 520.79 calcd $[M]^+$, found 520.39 $[M]^+$.

1b: Compound **1a** (1.53 g, 2.38 mmol) was dissolved in 30 mL THF and was then treated with NaOH (1 g/ 10 mL H_2O). The resultant mixture was vigorously stirred and refluxed for 4 days at 70 °C. The organic layer was washed with 1N HCl (3 x 50 mL), dried over anhydrous $MgSO_4$ and was evaporated using a rotary evaporator. It was then purified by column chromatography using $CHCl_3$ as an eluent to give colorless oil of **1b**

(1.29 g, 87%), which solidifies to a white low melting solid upon cooling; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.21-1.61 (m, 36H; CH_2), 1.81-1.83 (m, 6H; OCH_2CH_2), 2.02 (q, ^3J (H, H) = 6.8 Hz, 6H; $=CHCH_2$), 4.02 (q, ^3J (H, H) = 5.8 Hz, 6H; OCH_2), 4.92-4.97 (m, 6H; $=CH_2$), 5.79-5.84 (m, 3H; $=CHCH_2$), 7.32 (s, 2H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.13, 26.48, 29.36, 29.57, 29.69, 29.79, 29.87, 29.96, 30.74, 33.15, 34.23, 63.50, 69.57, 73.94, 108.93, 114.34, 114.54, 124.17, 126.30, 139.38, 143.47, 153.24, 171.90 [only 14 out of 18 aliphatic carbons could be found as separate signals due to merging]; MS (MALDI-TOF, matrix; dithranol): 649.94 calcd $[M + Na]^+$, found 649.89 $[M + Na]^+$.

2b: The reaction and work-up procedures were followed as similar to that of compound **1b**. The crude oil was purified by column chromatography using $CHCl_3$ as an eluent to give colorless oil of **2b** (1.1g, 87%); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.93-0.98 (m, 18H; CH_3), 1.35-1.36 (m, 12H; CH_2), 1.46-1.61 [m, 13H; CH_2 (12) and OCH_2CH (1)], 1.79-1.80 (m, 2H; OCH_2CH), 3.91-3.99 (m, 6H; OCH_2), 7.36 (s, 2H; ArH); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.52, 11.59, 14.51, 14.55, 23.50, 23.54, 24.05, 24.23, 29.50, 29.69, 30.83, 30.93, 39.96, 41.04, 71.69, 76.38, 108.41, 123.87, 143.54, 153.45, 172.54; MS (MALDI-TOF, matrix; dithranol): 529.74 calcd $[M + Na]^+$, found 529.57 $[M + Na]^+$.

1c: Compound **1b** (1.29 g, 2.06 mmol) was taken in a 100 mL round bottomed flask under N_2 atmosphere, 1mL of $SOCl_2$ was added and the mixture was stirred at RT for 30 min. The excess $SOCl_2$ was distilled off under reduced pressure. Dry DCM (3 x10 mL) was added and distilled to remove the remaining $SOCl_2$. In a 200 mL round bottomed flask under N_2 atmosphere was taken ethylene diamine (in excees) in dry DCM (10 mL) and the solution was kept at 0 °C. The acid chloride was then added dropwise for 30 min. The mixture was then gradually brought to RT and stirred for 12 h. The reaction mixture was washed with 1 (N) HCl (3 x 50 mL) extracted with $CHCl_3$, dried over anhydrous $MgSO_4$ and evaporated to get a low melting white colored solid (1.1 g, 80%); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.32-1.78 (m, 36H; CH_2), 1.82-1.86 (m, 6H, OCH_2CH_2), 2.07 (q, ^3J (H, H) = 6.9 Hz, 6H; $=CHCH_2$), 4.03-4.07 (m, 8H; OCH_2 and CH_2NH_2), 4.09-4.16 (m, 2H; CH_2NHCO), 4.95-5.03 (m, 6H, $=CH_2$), 5.81-5.87 (m, 3H; $=CHCH_2$), 7.33 (s, 2H; ArH); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.82, 26.49, 26.56, 29.37, 29.59, 29.61, 29.81, 29.88, 29.92, 29.97, 30.02, 30.10, 30.76, 34.22, 40.04, 40.97, 51.14, 58.81, 59.56, 69.73, 106.38, 114.53, 114.54, 126.29, 128.92, 139.56, 141.54, 153.38, 168.72; MS (MALDI-TOF, matrix; dithranol): 669.05 calcd $[M]^+$, found 669.23 $[M\ ]^+$.

1: Compound **1c** (1.1 g, 1.64 mmol) was transferred to a 100 mL round bottomed flask containing 1,4,5,8 naphthalenetetracarboxylic anhydride (0.15 g, 0.54 mmol) in 20 mL DMF. The reaction mixture was heated at 140 °C for 6 h and cooled to RT. An orange colored solid appeared, after cooling the flask in a refrigerator for 30 min. The solution was filtered and and the product was subjected to column chromatography using [silica gel, $CHCl_3$/MeOH 50:1] to obtain a cream colored solid of **1** (0.83 g, 64 %); m.p. 179-180 °C; ^1H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.32\text{-}1.59$ (m, 72H; CH_2), 1.74-1.85 (m, 12H; OCH_2CH_2), 2.06 (q, ^3J (H, H) = 7.0 Hz, 6H; $=CHCH_2$), 3.89-3.90 (m, 4H; $NHCH_2$), 3.95 (t, ^3J (H, H) = 6.5 Hz, 4H; OCH_2), 3.98 (t, ^3J (H, H) = 6.4 Hz, 8H; OCH_2), 4.56 (t, ^3J (H, H) = 5.2 Hz, 4H; NCH_2), 4.94-5.03 (m, 12H; $=CH_2$), 5.83-5.84 (m, 6H; $=CHCH_2$), 6.74 (t, ^3J (H, H) = 5.0 Hz, 2H; $NHCH_2$), 6.92 (s, 4H; ArH), 8.76 (s, 4H; ArH); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 23.92$, 23.99, 26.53, 26.81, 27.03, 27.28, 27.35, 27.41, 27.53, 28.17, 29.35, 29.77, 30.01, 31.68, 34.22, 38.07, 67.01, 69.55, 71.31, 74.67, 74.88, 103.24, 112.0, 114.54, 124.41, 124.72, 126.29, 126.85, 126.95, 128.99, 137.06, 138.82, 150.85, 153.39, 161.33, 163.87, 165.46 [16, instead of 12 aromatic carbon signals were found in solution]; MS (MALDI-TOF, matrix; dithranol): 1571.25 calcd $[M+H]^+$, found 1571.52 $[M+H]^+$. Anal. Calcd for $C_{98}H_{144}N_4O_{12}$: C 74.96, H 9.24, N 3.57; Found C 75.01, H 9.22, N 3.61.

2: Compound **2c** was obtained as a colorless oil (0.91 g, 76%) by following similar procedure that of **1c**. From TLC a single product was confirmed. The oil was not further purified and was used directly for the next step. The condensation reaction of **2c** with 1,4,5,8 naphthalenetetracarboxylic anhydride was done in a similar fashion to that of **1**. After usual work-up the crude solid was recrystallized from a 1:1 (v/v) mixture of CH_2Cl_2/CH_3OH to obtain **2** as a pale yellow colored solid (0.73 g, 66%); m.p. 169-170 °C. ^1H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.89\text{-}0.94$ (m, 36H; CH_3), 1.31-1.32 (m, 24H; CH_2), 1.41-1.76 (m, 30H; CH_2 and OCH_2CH), 3.81-3.89 (m, 16H; OCH_2 and $NHCH_2$), 4.54 (t, ^3J (H, H) = 4.5 Hz, 4H; NCH_2), 6.77 (t, ^3J (H, H) = 4.8 Hz, 2H; $NHCH_2$), 6.91 (s, 4H; ArH), 8.72 (s, 4H; ArH); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.51, 14.51, 14.61, 14.80, 23.54, 24.08, 24.24, 29.53, 29.73, 30.27, 31.52, 40.03, 40.21, 40.64, 41.05, 70.76, 71.67, 76.36, 105.82, 126.29, 126.99, 127.29, 129.22, 141.23, 153.63, 163.90, 168.90; MS (MALDI-TOF, matrix; dithranol): 1330.86 calcd $[M+H]^+$, found 1330.50 $[M+H]^+$. Anal. Calcd for $C_{80}H_{120}N_4O_{12}$: C 72.25, H 9.09, N 4.21; Found C 72.29, H 9.07, N 4.26.

Gelation test

The gelator and the solvent were put in a screw capped sample vial and heated until the solid was dissolved. The sample vial was cooled to RT. The formation of the gels was evaluated by the "stable-to-inversion of a test tube" method. Gelation ability of **1** was evaluated in 22 common organic solvents. Stable and transparent gels were formed in benzene, toluene, *p*-xylene, anisole, cyclohexane, methylcyclohexane, hexane, decane, diphenylether and decalin. Whereas, ethanol, butanol, propanaol, iso-propanol, ethanol, dimethylsulfoxide (DMSO), dimethylformamide (DMF), dioxane, acetonitrile, acetone and ethylacetate gave opaque gels. No gels were formed in solvents like methanol, pyridine, chloroform, dichloromethane and tetrahydofuran. Most of the gels could be obtained by using as low as 0.5 mg/ml of **1**.

UV-Vis spectra and TEM image of 1

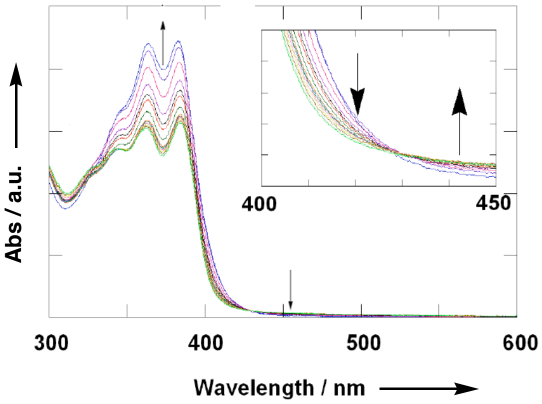


Figure S1. UV-Vis spectra of **1** at various temperatures, showing the destacking of the naphthalenediimide moieties due to heating ([**1**] = 4.0 mM in cyclohexane, 25 °C~80 °C).

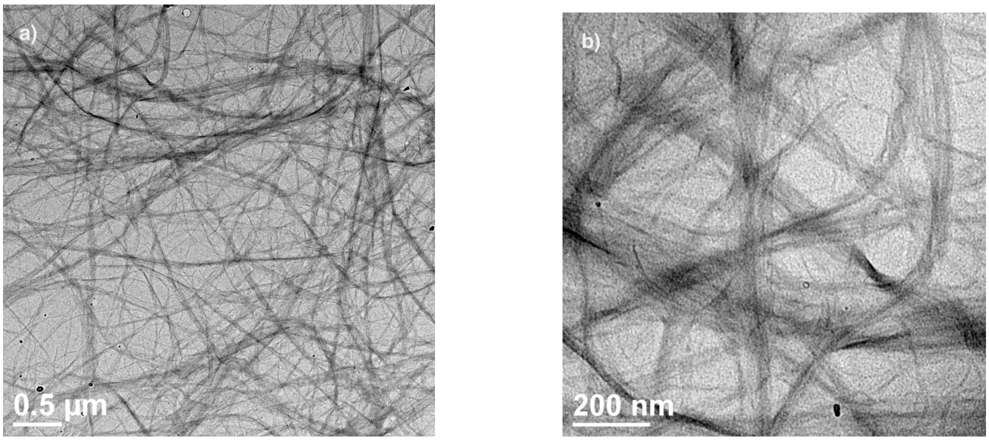


Figure S2. TEM images of organogel **1** at various resolutions, showing the long 1-D fibers in cyclohexane (4 mM).

Photograph showing a reversible chromatic change of the 1・3f complex:

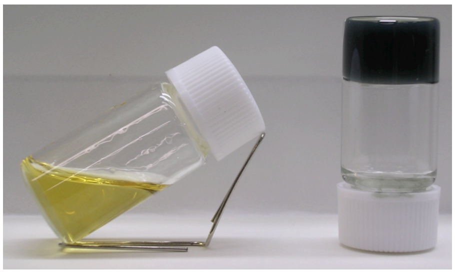


Figure S3. Photograph showing a reversible chromatic change of the **1**・**3f** complex on the sol-gel phase transition upon heating and cooling processes ([**1**・**3f**] = 3.5 mM in cyclohexane).

Molecular modeling (using the Discover 3/Insight II 98.0 software): The restraints were applied according to the literature surveys of the crystal structures of naphthalenediimide moiety.

Restraints: π-π stacking 3.5 Å between naphthalenediimides and naphthalenediimide-dihydroxynaphthalene**;** H-bonding distances for N---O in **1** and O---O in **1**・**3f** complex were restrained at 2.8 and 3.2 Å, respectively.

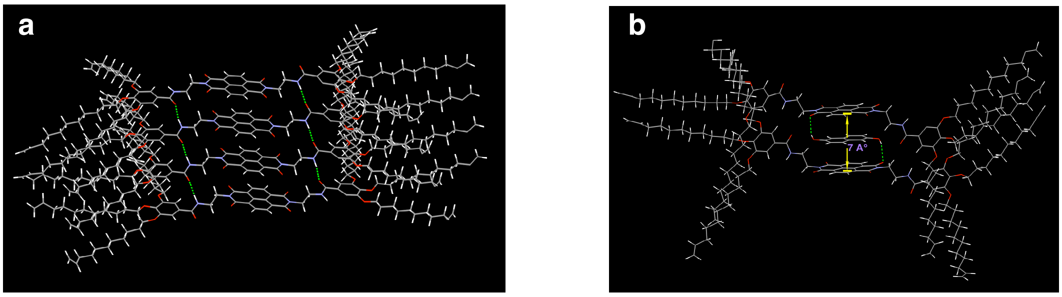


Figure S4. (a) 1-D stacking of **1** utilizing π-stacking of naphthalenediimides, H-bonding between the amide groups and van der Waals interaction; (b) The energy-minimized structure of the **1** • **3f** complex shows a O–H---O angle of 142-145° signifying a weak-H-bonding along the 1-D gel matrix; Green dashed lines indicate the N–H---O H-bonding interactions between the amide moieties in case of **1** and O–H---O interactions in **1** • **3f** complex, respectively.

ATR-FTIR spectra

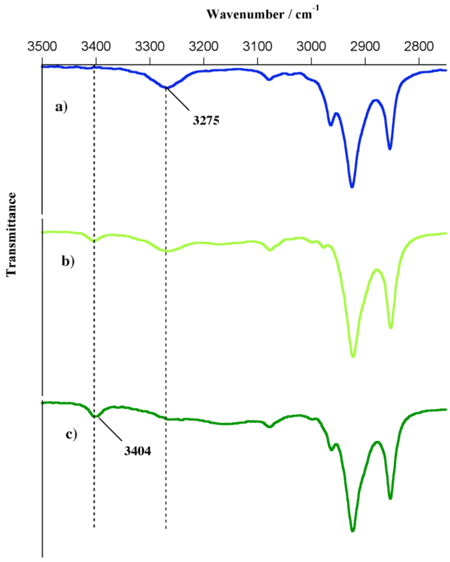


Figure S5. ATR-FTIR spectra of the xerogels in the region of 3500-2750 cm^{-1} of: a) **1**, showing the characteristic H-bonded amide group (νN–H) at 3275 cm^{-1}, due to the formation of intermolecular H-bonded chains (N–H---O=C) [Please refer to Figure S4 (a), green-dashed lines]; b) **1** in presence of 0.5 equivalents of **3f**; and c) **1• 3f** (1:1), showing the absence of H-bonded amide groups (at 3275 cm^{-1}) and arrival of a new peak at 3404 cm^{-1} due to the formation of non H-bonded amide groups as a result of the intercalation by **3f** and disruption of the intermolecular H-bonding [Please refer to Figure S4 (b)].

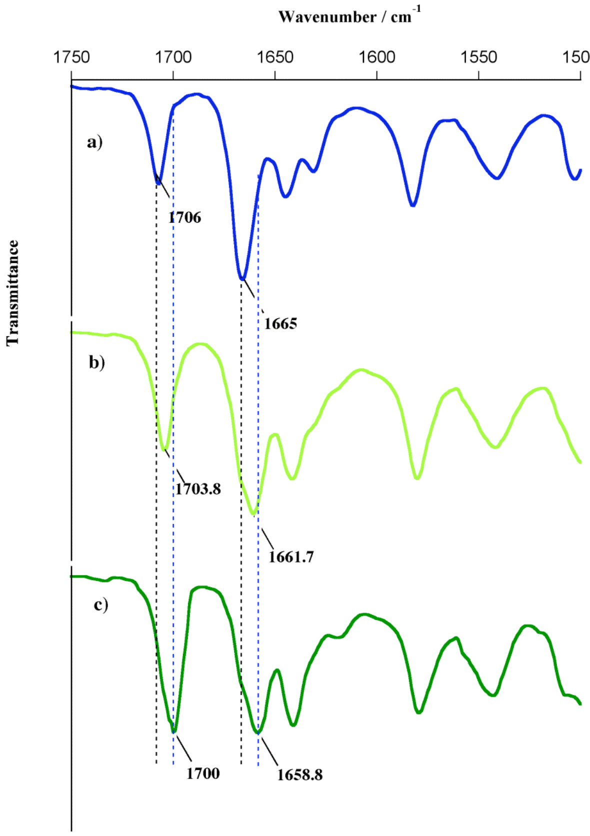


Figure S6. ATR-FTIR spectra of the xerogels in the region of 1750-1500 cm^{-1} of: a) **1**, spectra showing the symmetrical and asymmetrical carbonyl group vibrations of naphthalenediimide moiety at 1706 and 1665 cm^{-1}; b) **1** in presence of 0.5 equivalents of **3f**; and c) **1• 3f** (1:1), showing the shifts of the carbonyl group vibration of naphthalenediimide moiety to 1700 and 1658.8 cm^{-1} as a result of the H-bonding with the donor **3f** moiety [Please refer to Figure S4 (b), green-dashed lines].