Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C
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Blends made from *N*-salicylidene aniline sulfonate derivatives and a polyampholyte matrix: *in situ* synthesis *vs.* solution mixing

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Experimental

Starting materials

Solvents (HPLC grade methanol from Prolabo; DMSO d_6 99.98% D) and reagents (sodium hydroxide analytical grade from Fisher Scientific, salicylaldehyde 99%, 5-chlorosalicylaldehyde 98% from Acros Organics, sulfanilic acid from Sigma-Aldrich, 3-aminobenzenesulfonic acid from Fluka) were obtained commercially and used as received. The polymer matrix *N,N*(diallylhexyl)-*alt*-maleic acid (**CopoC$_6$H**) was synthesized following previously reported procedures.[1]

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 MHz spectrometer with DMSO as the internal standard. Infrared spectra were obtained using a Equinox 55 from Bruker on KBr disks. Diffuse reflectance spectra were recorded on a Varian Cary 5E spectrophotometer using PTFE as reference. Powder X-ray diffractograms were obtained using a Siemens D5000 X-ray diffractometer, with a Cu anticathode (λ-K_α = 1.5418 Å).

Synthesis of salicylidene aniline sulfonate derivatives

General synthesis: Aminobenzene sulfonic acid (2.89 mmol) and NaOH (0.116 g, 2.89 mmol) are dissolved in 20 mL MeOH. Vigorous stirring is maintained until complete solubilisation of the reagents. Salicylaldehyde (2.89 mmol) is then added dropwise to the solution. Temperature is increased to reflux (80°C) and stirring is maintained overnight. A yellow solid is formed and then filtrated. Purification is performed by re-crystallisation in hot MeOH. Pure yellow crystals are obtained.

1Na: yield: 58%. ^{1}H NMR (d^6-DMSO): 13.04 (s, 1H), 8.99 (s, 1H), 7.71 (d, 1H, $^3J_{H\text{-}H}$ = 7.92 Hz), 7.57 (m, 2H), 7.38 (m, 3H) 6,98 (t, 2H, $^3J_{H\text{-}H}$ = 7.71 Hz) ppm; FTIR (KBr disk $\bar{\nu}$ (cm^{-1}): 1620 (C=N), 1120 (S=O), 725 (S-O$^-$), 662 (C-S); *Anal.* Calc for $C_{13}H_{10}NSO_4Na$: C 52.17, H 3.37, N 4.68, Found: 52.32, H 3.33, N 4.72 %

2Na: yield: 66%. ^{1}H NMR (d^6-DMSO): 13.04 (s, 1H), 8.98 (s, 1H), 7.68 (d, 3H, $^3J_{H\text{-}H}$ = 8.43 Hz), 7.40 (m, 3H), 6,98 (t, 2H, $^3J_{H\text{-}H}$ = 7.38 Hz) ppm, FTIR (KBr disk) $\bar{\nu}$ (cm^{-1}): 1625 (C=N), 1134 (S=O), 730 (S-O$^-$), 651 (C-S), *Anal.* Calc for $C_{13}H_{10}NSO_4Na$: C 52.17, H 3.37, N 4.68, Found: 51.95, H 3.50, N 4.80 %

3Na: yield of 58%. 13.04 (s, 1H), 8.98 (s, 1H), 7.80 (d, 1H, $^3J_{H\text{-}H}$ = 2.7 Hz), 7.58 (m, 2H), 7.40 (m, 3H), 7.01 (d, 2H, $^3J_{H\text{-}H}$ = 8.82 Hz) ppm; FTIR (KBr disk) $\bar{\nu}$ (cm^{-1}): 1618 (C=N), 1114 (S=O), 748 (S-O$^-$), 628 (C-S) cm^{-1}; *Anal.* Calc for $C_{13}H_{9Cl}NSO_4Na$: C 46.19, H 2.72, N 4.20, Found: 46.50, H 3.01, N 4.02 %

4Na: yield: 66%. 13.04 (s, 1H), 8.96 (s, 1H), 7.76 (d, 1H, $^3J_{H\text{-}H}$ = 2.73 Hz), 7.67 (d, 2H, $^3J_{H\text{-}H}$ = 4.68 Hz), 7.44 (d, 1H, $^3J_{H\text{-}H}$ = 11.55 Hz), 7.35 (d, 2H, $^3J_{H\text{-}H}$ = 4,71) 6,98 (d, 1H, $^3J_{H\text{-}H}$ = 8.85 Hz) ppm; FTIR (KBr disk) $\bar{\nu}$ (cm^{-1}): 1622 (C=N), 1134 (S=O), 746 (S-O$^-$), 677 (C-S); *Anal.* Calc for $C_{13}H_{9Cl}NSO_4Na$: C 46.19, H 2.72, N 4.20, Found: 46.07, H 2.75, N 4.24 %

Hybrid materials

Method I: mixing

CopoC$_6$H (50 mg, 0.1607mmol repetitive unit) are dissolved in 250 mL MeOH. Different amounts of salicylidene aniline sulfonate derivatives (from 0.05 to 2.0 mol equiv. per repetitive unit of polymer) are added to the solution and stirring is maintained at 30°C during 24h. The solvent is removed under vacuum and a yellow powder is obtained.

Method II: *in situ* synthesis

Preparation of aminobenzene sulfonate/**CopoC$_6$H$_2$$^+$**:

CopoC$_6$H (2.00 g, 7.404 mmol repetitive unit) is dissolved in 200 mL MeOH. Aminobenzene sulfonic acid (1.28 g, 8.145 mmol) is added to the solution and vigorous stirring is maintained room temperature (5 h for 3-aminobenzenesulfonic acid, 3 h for 4-aminobenzenesulfonic acid). The solution is filtered out to remove the excess of sulfanilic acid. The solvent is removed under vacuum and a white product is obtained.

3-aminobenzenesulfonate/**CopoC$_6$H$_2$$^+$**: yield: 51%, ^{1}H NMR (d^6-DMSO): 6.94 (m, 1.10 H), 6.77 (d, 0.55 H, $^3J_{H\text{-}H}$ = 7.61 Hz), 6.51 (d, 0.55 H, $^3J_{H\text{-}H}$ = 8.20 Hz), 3.33 (s, 8H), 1.53 (s, 2H), 1.23 (6H), 0.85 (s, 3H) ppm; FTIR (KBr disk) $\bar{\nu}$ (cm^{-1}): 3365 (NH$_2$), 1599 (N$^+$-H), 1105 (S=O), 785 (S-O$^-$), 690 (C-S)

4-aminobenzenesulfonate/**CopoC$_6$H$_2$$^+$**: yield: 60%, ^{1}H NMR (d^6-DMSO): 7.27 (d, 1.30 H, $^3J_{H\text{-}H}$ = 8.43 Hz), 6.46 (d, 1.30 H, $^3J_{H\text{-}H}$ = 8.46), 3.35 (s, 5H), 3.04 (s, 3H), 1.54 (s, 2H), 1.23

(6H), 0.85 (s, 3H) FTIR (KBr disk) $\bar{\nu}$ (cm^{-1}): 3365 (NH_2), 1599 (N^+-H), 1119 (S=O), 831 (S-O^-), 694 (C-S)

Synthesis of salicylidene aniline sulfonate in **Copo$C_6H_2^+$**: aminobenzene sulfonate/**Copo$C_6H_2^+$** (100 mg, 0.2 mmol) is solubilized in 50 mL MeOH. Salicylaldehyde (0.31 mmol) is added to the solution and kept stirred during 6 h at ambient temperature. MeOH is removed under vacuum. The crude product is washed three times with dichloromethane (20 mL) in order to remove the excess of salicylaldehyde.

i1: yield: 42%, %, ^{1}H NMR (d^6-DMSO): 8.99 (s, 0.30 H), 7.69 (m, 0.30 H), 7.57 (m, 0.60 H), 7.41 (m, 0.90 H), 6.95 (m, 0.90 Hz), 3.16 (s, 5 H), 3.05 (s, 3 H), 1.53 (s, 2 H), 0.84 (s, 3 H); FTIR (KBr disk) $\bar{\nu}$ (cm^{-1}): 1620 (C=N), 1591 (N^+-H), 1105 (S=O), 723 (S-O^-), 669 (C-S)

i2: yield: 38%, ^{1}H NMR (d^6-DMSO): 8.98 (s, 0.40 H), 7.67 (m, 1.20 H), 7.40 (m, 1.20 H), 6.98 (t, 0.80 H, $^3J_{H\text{-}H}$ = 7.59 Hz), 3.17 (s, 7 H), 3.04 (s, 3 H), 1.53 (s, 2 H), 0.84 (s, 3 H) FTIR (KBr disk) $\bar{\nu}$ (cm^{-1}): 1620 (C=N), 1595 (N^+-H), 1120 (S=O), 725 (S-O^-), 640 (C-S)

i3: yield: 39% %, ^{1}H NMR (d^6-DMSO): 8.97 (s, 0.30 H), 7.80 (d, 0.30 H, $^3J_{H\text{-}H}$ = 2.92 Hz), 7.58 (m, 0.60 H), 7.42 (m, 0.90 H), 6.95 (m, 0.90 H), 3.33 (s, 5 H), 3.17 (s, 3 H), 1.52 (s, 2 H), 1.20 (s, 6H), 0.84 (s, 3 H) FTIR (KBr disk) $\bar{\nu}$ (cm^{-1}): 1620 (C=N), 1107 (S=O), 744 (S-O^-), 615 (C-S)

i4: yield: 39% %, ^{1}H NMR (d^6-DMSO): 8.96 (s, 0.30 H), 7.76 (d, 0.30 H, $^3J_{H\text{-}H}$ = 2.67 Hz), 7.68 (d, 0.60 H), 7.44 (dd, 0.30 H, $^3J_{H\text{-}H}$ = 17.85, $^3J_{H\text{-}H}$ = 2.7 Hz), 7.36 (d, 0.60 H, $^3J_{H\text{-}H}$ = 8.37 Hz), 7.00 (d, 0.30 H, $^3J_{H\text{-}H}$ = 8.85 Hz), 3.17 (s, 8 H), 3.04 (s, 3 H), 1.53 (s, 2 H), 1.20 (s, 6 H) 0.84 (s, 3 H); FTIR (KBr disk) $\bar{\nu}$ (cm^{-1}): 1620 (C=N), 1119 (S=O), 750 (S-O^-), 669 (C-S)

Reference

1. a) F. Rullens, N. Deligne, A. Laschewsky and M. Devillers, *J. Mater. Chem.,* 2005, **15**, 1668 b) F. Rullens, M. Devillers and A. Laschewsky, *J. Mater. Chem.,* 2004, **14**, 3421 c) F. Rullens, A. Laschewsky and M. Devillers, *Chem. Mater.* 2006, **18**, 771 d) F. Rullens, M. Devillers and A. Laschewsky, *Macromol. Chem. Phys.,* 2004, **205**, 1155

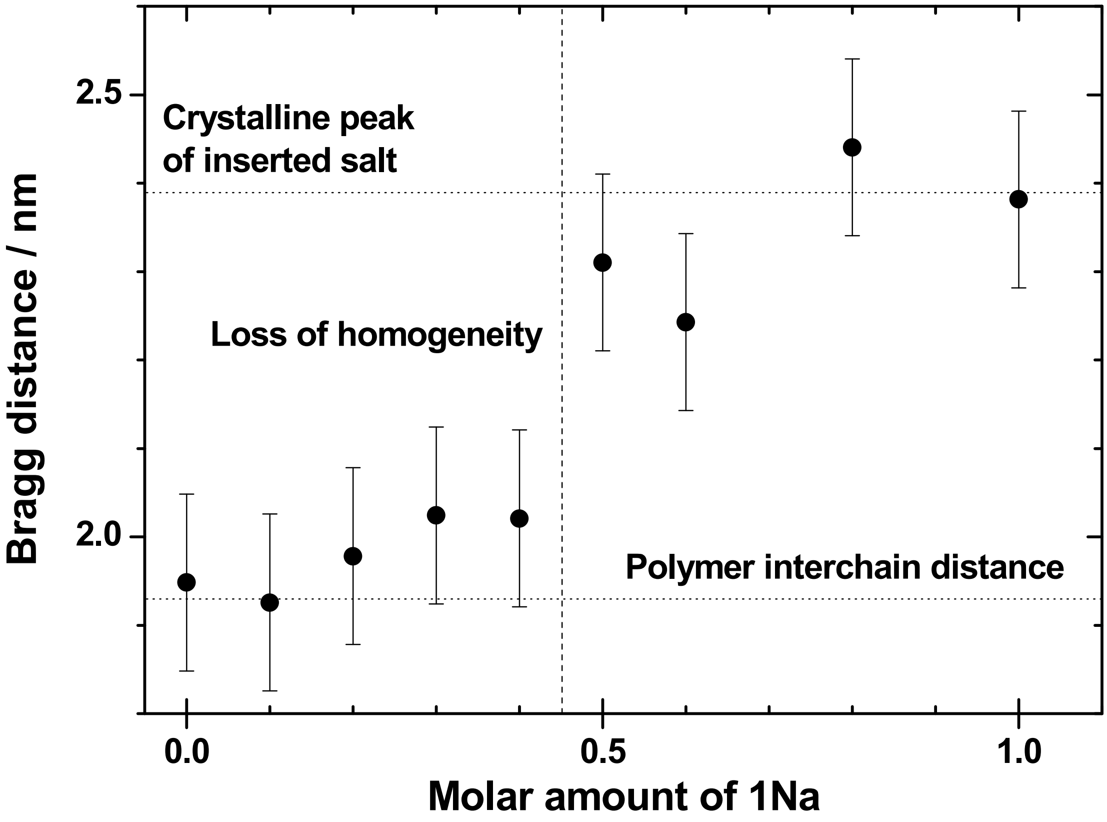

Figure S1. Evolution of the Bragg distance related to the most intense diffraction peak for **1Na** inserted in **CopoC$_6$H** in function of the loading of the host matrix: the loss of homogeneity is defined by the emergence of crystalline peaks of **1Na**.

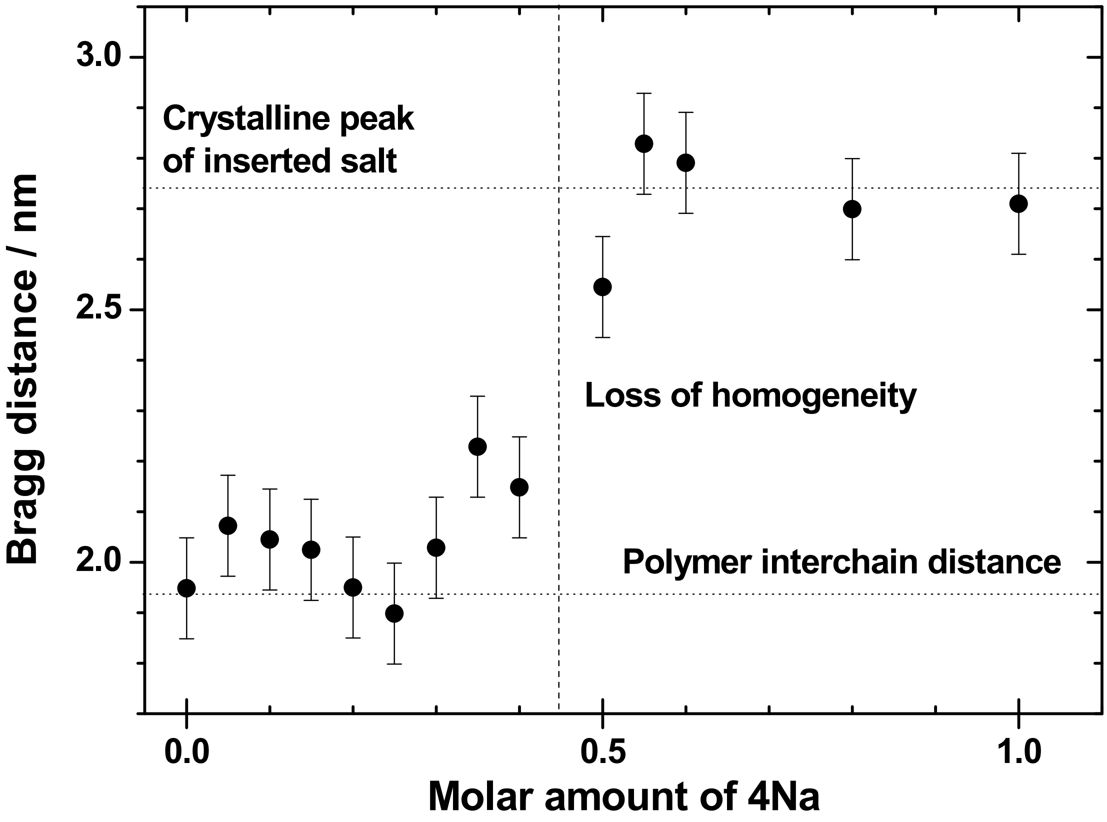

Figure S2. Evolution of the Bragg distance related to the most intense diffraction peak for **2Na** inserted in **CopoC$_6$H** in function of the loading of the host matrix: the loss of homogeneity is defined by the emergence of crystalline peaks of **2Na**.

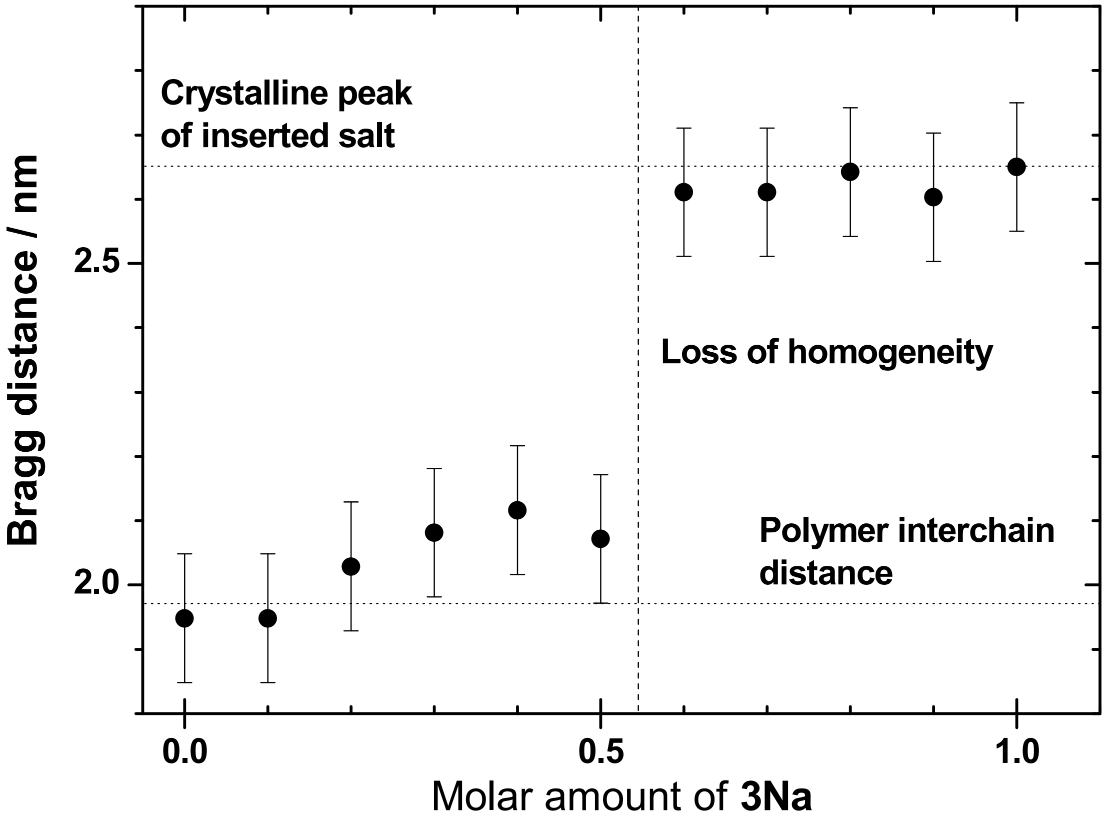

Figure S3. Evolution of the Bragg distance related to the most intense diffraction peak for **3Na** inserted in **CopoC$_6$H** in function of the loading of the host matrix: the loss of homogeneity is defined by the emergence of crystalline peaks of **3Na**

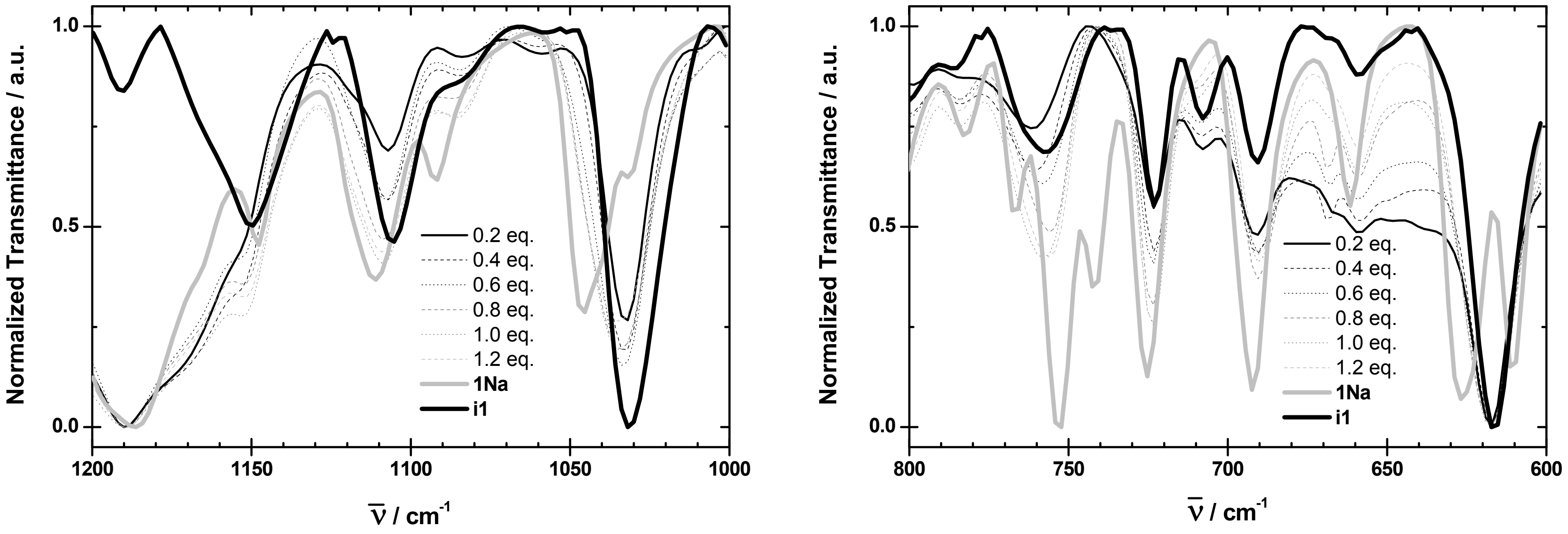

Figure S4. Comparison between infrared spectra of **1Na** (grey) and **i1** (black) and evolution of infrared spectra with the loading of **1Na** inserted in **CopoC$_6$H**: Left: SO_2 symmetric stretching; Right: SO^- and CS stretching

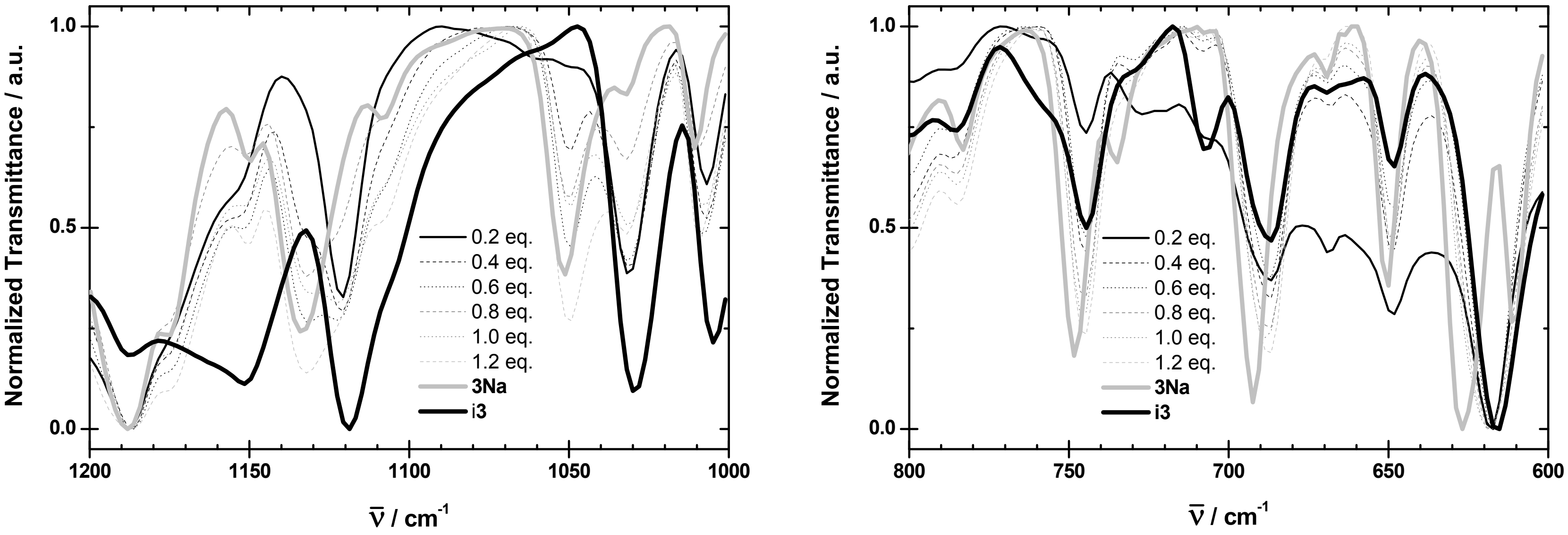

Figure S5. Comparison between Infrared spectra of **3Na** (grey) and **i3** (black) and evolution of infrared spectra with the loading of **3Na** inserted in **CopoC$_6$H**: Left: SO$_2$ symmetric stretching; Right: SO$^-$ and CS stretching

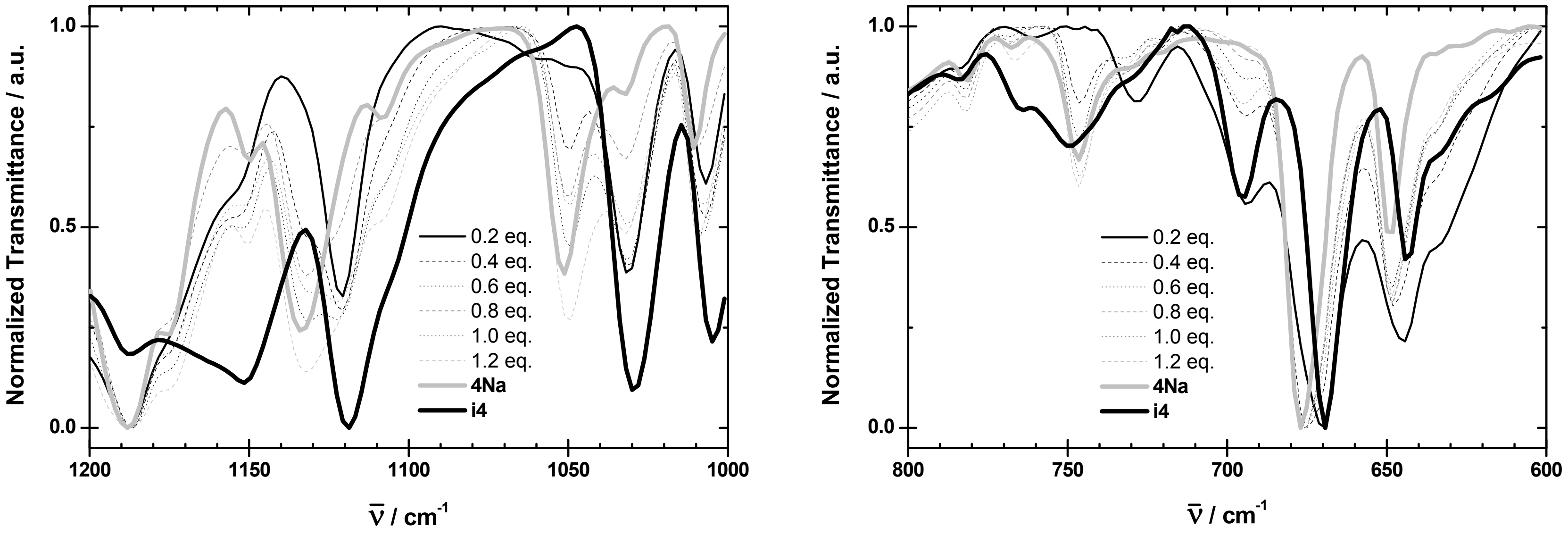

Figure S6. Comparison between Infrared spectra of **4Na** (grey) and **i4** (black) and evolution of infrared spectra with the loading of **4Na** inserted in **CopoC$_6$H**: Left: SO_2 symmetric stretching; Right: SO^- and CS stretching

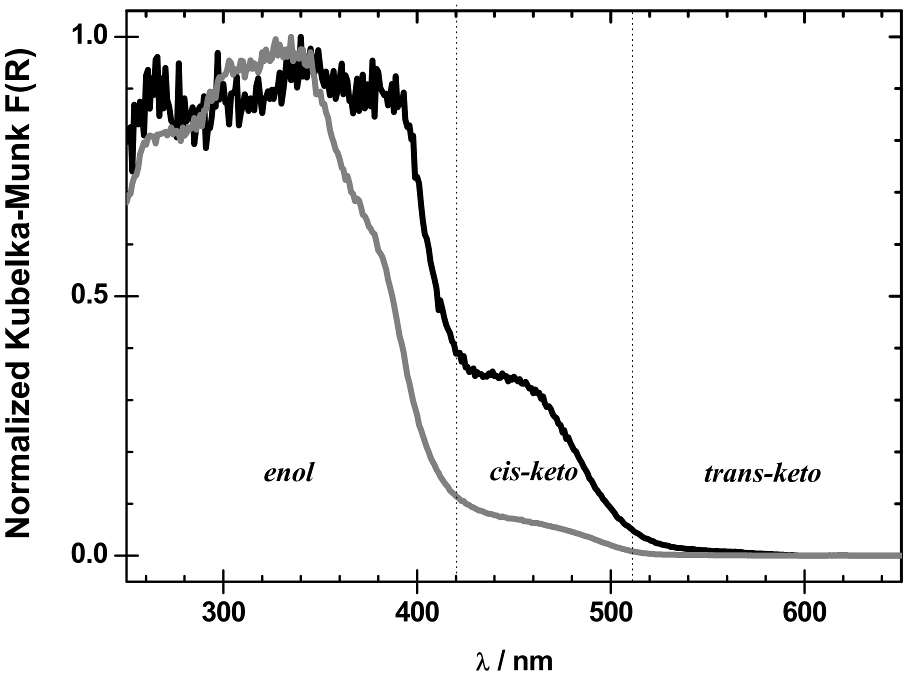

Figure S7. Diffuse reflectance spectra of **i1** (grey) in comparison to **1Na** (black).

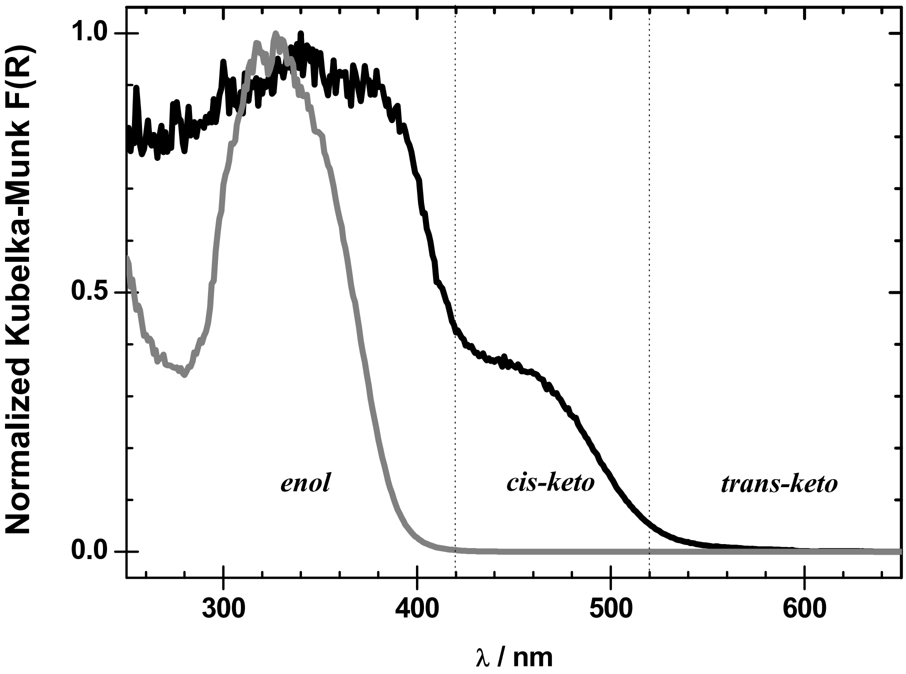

Figure S8. Diffuse reflectance spectra of **i2** (grey) in comparison to **2Na** (black).

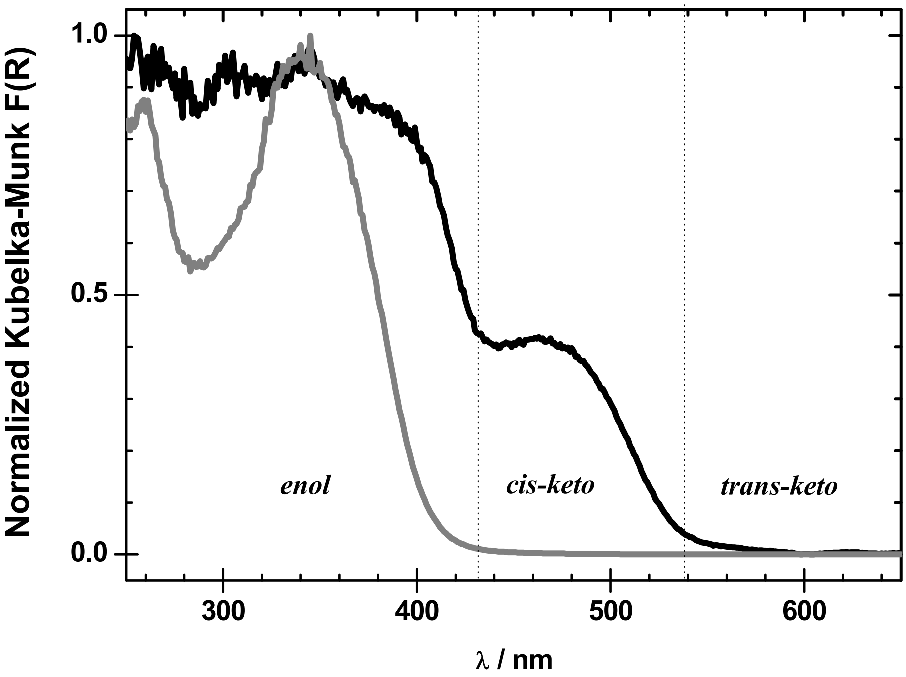

Figure S9. Diffuse reflectance spectra of **i4** (grey) in comparison to **4Na** (black).

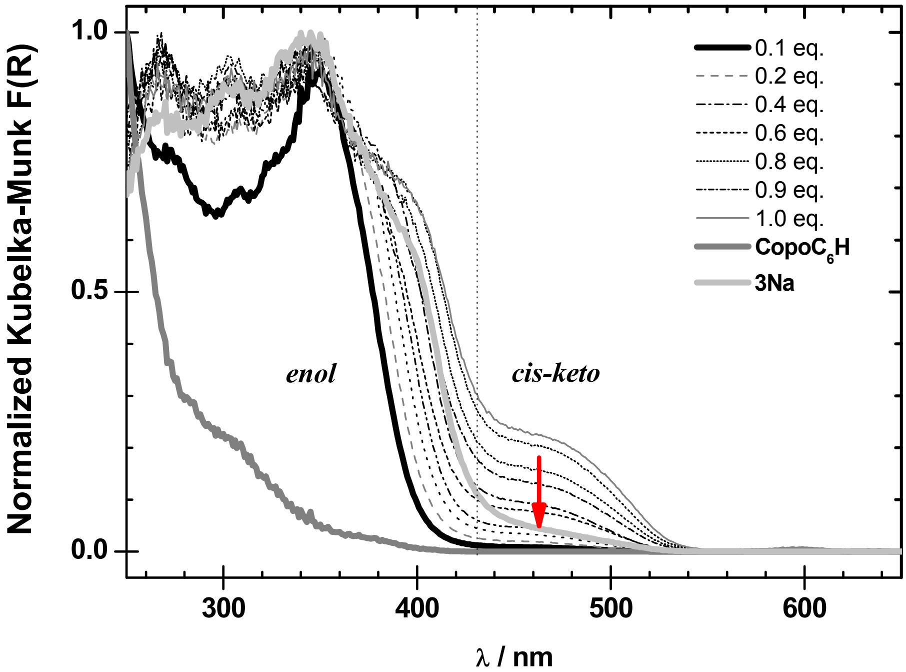

Figure S10. Evolution of diffuse reflectance spectra of hybrid materials obtained by mixing with the loading of **3Na** in **CopoC$_6$H**.

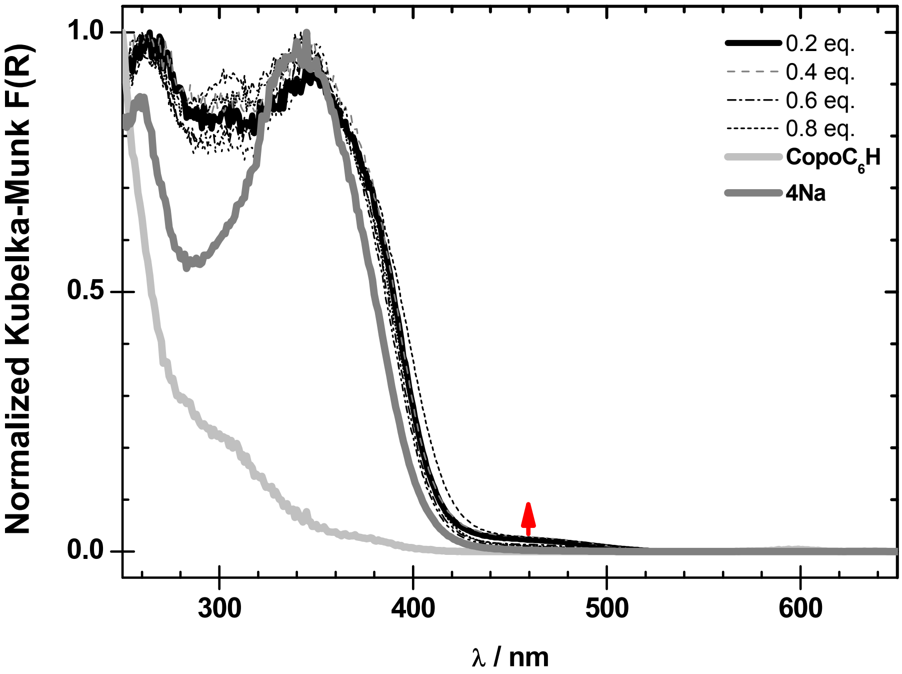

Figure S11. Evolution of diffuse reflectance spectra of hybrid materials obtained by mixing with the loading of **4Na** in **CopoC$_6$H**.