

SUPPORTING INFORMATION for

Insight into the Supramolecular Organization of Columnar Assemblies with Phototunable Chirality

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Synthetic procedures and characterization data

¹H NMR studies

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X-ray density calculations

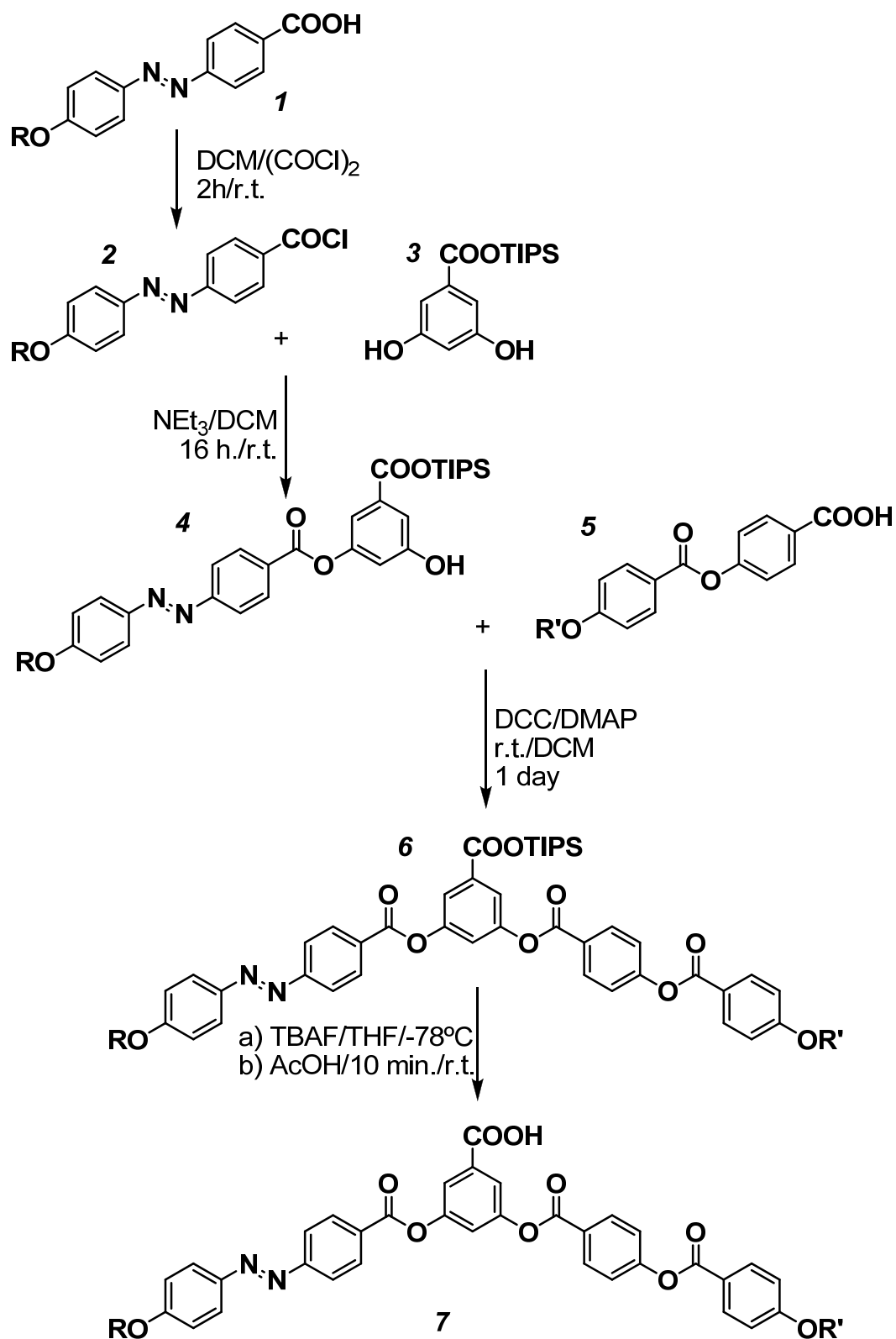
UV/Vis spectra

CD studies

General experimental details

Synthetic procedures and characterization data

The synthetic procedures followed for the preparation of the V-shaped acids are outlined in the following scheme



Compounds 1 and 2, {Vera, 2007 #84; Vera, 2010 #69} **3** {Xu, 2004 #105} and **5** {Barberá, 2006 #85} were prepared as described elsewhere.

Compounds 4. 7 mmol of compound **3** were diluted with 100 mL of dry DCM. Then, 9 mmol of TEA were added via syringe under argon atmosphere. Then, a solution of 7 mmol of the corresponding acid chloride **2** in dry DCM was added drop wise. The reaction mixture was stirred for 15 hours at room temperature. Then, it was extracted with water and DCM. The organic layer was evaporated, and the crude product was purified by column chromatography on silica gel (Hexanes/Ethyl acetate, 8:2). Compounds **4** are red solids. Yields: 30 %. *R_f*: 0.3 (silicagel, hexanes/ethyl acetate, 8:2)

4 (A12): ¹H-NMR (400 MHz, CDCl₃): δ 8.32 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.97 (d, *J* = 8.4 Hz, Ar-*H*), 7.95 (d, 8.8 Hz, 2H, Ar-*H*), 7.49 (dd, *J* = 2.0, *J* = 1.6 Hz, 1H, Ar-*H* central ring *p*-COOTIPS), 7.46 (dd, *J* = 2.0 Hz, *J* = 1.6 Hz, 1H, Ar-*H* central ring *o*-COOTIPS, *p*-OH), 7.02 (d, *J* = 8.8 Hz, Ar-*H*), 7.00 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, Ar-*H* *o*-COOTIPS, *o*-OH), 4.06 (t, *J* = 6.4 Hz, 2H, -OCH₂CH₂-), 1.87-1.79 (m, 2H, -OCH₂CH₂CH₂-), 1.52-1.43 (m, 2H, -OCH₂CH₂CH₂-), 1.40-1.22 (m, 16H, -CH₂-), 1.27 (t, *J* = 7.2 Hz, 3H, -CH₃-), 1.15 (d, *J* = 7.2 Hz, 18H, -CH(CH₃)₂), 0.88 (t, *J* = 6.4 Hz, 3H, -O(CH₂)₁₁CH₃). FT-IR (nujol): 3500-3100 cm⁻¹ (OH), 1734 cm⁻¹ (C=O), 1679 cm⁻¹ (C=O TIPS), 1255 cm⁻¹ (C_{Ar}-O).

4 (A(S)10*): ¹H-NMR (400 MHz, CDCl₃): δ 8.31 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.96 (d, *J* = 8.4 Hz, Ar-*H*), 7.95 (d, 8.8 Hz, 2H, Ar-*H*), 7.47 (dd, *J* = 2.0, *J* = 1.6 Hz, 1H, Ar-*H* central ring *p*-COOTIPS), 7.45 (dd, *J* = 2.0 Hz, *J* = 1.6 Hz, 1H, Ar-*H* *o*-COOTIPS, *o*-OH), 7.01 (d, *J* = 8.8 Hz, Ar-*H*), 6.99 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, Ar-*H* central ring *o*-COOTIPS, *p*-OH), 4.08 (t, *J* = 6.4 Hz, 2H, -OCH₂CH₂-), 1.92-1.82 (m, 1H, -CH-(CH₃)₂), 1.76-1.60 (m, 2H, -CH₂CH₂O-), 1.58-1.50 (m, 1H, -CH₂-CH(CH₃)-CH₂-), 1.39 (m, *J* = 7.2 Hz, 3H, -CH- TIPS), 1.38-1.24 (m, 3H, -CH₂-), 1.22-1.11 (m, 3H, -CH₂-), 1.12 (d, *J* = 7.2 Hz, 18H, -CH₃ TIPS), 0.96 (d, *J* = 6.8 Hz, 3H, -CH(CH₃)-), 0.86 (d, *J* = 6.4 Hz, 6H, -CH(CH₃)₂). FT-IR (Nujol): 3500-2900 cm⁻¹ (OH), 1739 cm⁻¹ (C=O), 1704 cm⁻¹ (C=O TIPS), 1290 cm⁻¹ (C-O) 1251 cm⁻¹ (C_{Ar}-O).

Compounds 6. A mixture of the corresponding 4-(4'-alkoxybenzoyloxy)benzoic acid, **5** (1 mmol), **4** (1 mmol) and DMAP (0.3 mmol) in DCM (40 mL) was stirred under argon atmosphere. The solution was cooled in an ice bath. Subsequently, N,N'-dicyclohexylcarbodiimide, DCC (1.1 mmol) was added. The mixture was stirred at room temperature overnight. The solution was filtered to remove the dicyclohexylurea formed. The solvent was removed under reduced pressure. The final product, **6**, was purified by flash chromatography on silica gel, eluting with hexane/ethyl acetate mixtures. Yield = 70 %. *R_f* (silicagel, hexanes/ethyl acetate, 9:1) = 0.66.

6 (A(S)10*-E(S)10*): ¹H-NMR (400 MHz, CDCl₃): δ 8.32 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 8.28 (d, *J* = 9.2 Hz, 2H, Ar-*H*), 8.14 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.98 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.96 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.86 (dd, *J* = 2.4 Hz, *J* = 2.0 Hz, 1H, Ar-*H* central ring *o*-COOTIPS), 7.84 (dd, *J* = 2.4 Hz, *J* = 2.0 Hz, 1H, Ar-*H* central ring *o*-COOTIPS), 7.45 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, 1H, Ar-*H* central ring *p*-COOTIPS), 7.38 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.02 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.98 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 4.09 (m, *J* = 7.6 Hz, 4H, -OCH₂CH₂-), 1.92-1.83 (m, 2H, -CH-(CH₃)₂), 1.76-1.60 (m, 4H, -OCH₂CH₂-), 1.58-1.50 (m, 2H, -CH₂-CH(CH₃)-CH₂-), 1.41 (m, *J* = 7.6 Hz, 3H, -CH- TIPS), 1.38-1.24 (m, 6H, -CH₂-), 1.22-1-11 (m, 6H, -CH₂-), 1.14 (d, *J* = 7.6 Hz, 18H, -CH₃ TIPS), 0.96 (d, *J* = 6.4 Hz, 6H, -CH(CH₃)-), 0.88 (d,

$J = 6.8$ Hz, 12H, $-\text{CH}(\text{CH}_3)_2$). FT-IR (Nujol): 1742 cm^{-1} (C=O rings), 1706 cm^{-1} (C=O TIPS), 1253 cm^{-1} ($\text{C}_{\text{Ar}}\text{-O}$).

6 (A12-E(S)10*): $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.34 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.29 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.16 (d, $J = 9.2$ Hz, 2H, Ar-*H*), 7.98 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.97 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 7.87 (dd, $J = 1.6$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *o*-COOTIPS), 7.85 (dd, $J = 1.6$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *o*-COOTIPS), 7.46 (dd, $J = 2.0$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *p*-COOTIPS), 7.39 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.03 (d, $J = 9.2$ Hz, 2H, Ar-*H*), 6.99 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 4.11-4.05 (m, $J = 7.6$ Hz, 4H, $-\text{OCH}_2\text{CH}_2-$), 1.92-1.80 (m, 3H, $-\text{CH}(\text{CH}_3)_2$), $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.62-1.45 (m, 3H, $-\text{CH}_2\text{-CH}(\text{CH}_3)\text{-CH}_2$, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.43 (t, $J = 8.0$ Hz, 3H, $-\text{CH}$ - TIPS), 1.40-1.21 (m, 19H, $-\text{CH}_2-$), 1.20-1.12 (m, 3H, $-\text{CH}_2-$), 1.15 (d, $J = 7.6$ Hz, 18H, $-\text{CH}_3$ TIPS), 0.96 (d, $J = 6.8$ Hz, 3H, $-\text{CH}(\text{CH}_3)_3$), 0.90-0.85 (m, 9H, $-\text{CH}(\text{CH}_3)_2$, $-\text{CH}_2\text{CH}_2\text{CH}_3$). FT-IR (Nujol): 1741 cm^{-1} (C=O rings), 1706 cm^{-1} (C=O TIPS), 1252 cm^{-1} ($\text{C}_{\text{Ar}}\text{-O}$).

6 (A(S)10*-E12): $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.34 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.29 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.16 (d, $J = 9.2$ Hz, 2H, Ar-*H*), 7.98 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.97 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 7.87 (dd, $J = 1.6$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *o*-COOTIPS), 7.85 (dd, $J = 1.6$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *o*-COOTIPS), 7.46 (dd, $J = 2.0$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *p*-COOTIPS), 7.39 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.03 (d, $J = 9.2$ Hz, 2H, Ar-*H*), 6.99 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 4.11-4.05 (m, $J = 7.6$ Hz, 4H, $-\text{OCH}_2\text{CH}_2-$), 1.92-1.80 (m, 3H, $-\text{CH}(\text{CH}_3)_2$), $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.62-1.45 (m, 3H, $-\text{CH}_2\text{-CH}(\text{CH}_3)\text{-CH}_2$, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.43 (t, $J = 8.0$ Hz, 3H, $-\text{CH}$ - TIPS), 1.40-1.21 (m, 19H, $-\text{CH}_2-$), 1.20-1.12 (m, 3H, $-\text{CH}_2-$), 1.15 (d, $J = 7.6$ Hz, 18H, $-\text{CH}_3$ TIPS), 0.96 (d, $J = 6.8$ Hz, 3H, $-\text{CH}(\text{CH}_3)_3$), 0.90-0.85 (m, 9H, $-\text{CH}(\text{CH}_3)_2$, $-\text{CH}_2\text{CH}_2\text{CH}_3$). FT-IR (Nujol): 1741 cm^{-1} (C=O rings), 1705 cm^{-1} (C=O TIPS), 1252 cm^{-1} ($\text{C}_{\text{Ar}}\text{-O}$).

6 (A12-E12): $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.34 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.29 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.16 (d, $J = 9.2$ Hz, 2H, Ar-*H*), 7.98 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.97 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 7.87 (dd, $J = 1.6$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *o*-COOTIPS), 7.85 (dd, $J = 1.6$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *o*-COOTIPS), 7.46 (dd, $J = 2.0$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *p*-COOTIPS), 7.39 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.03 (d, $J = 9.2$ Hz, 2H, Ar-*H*), 6.99 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 4.11-4.05 (m, $J = 7.6$ Hz, 4H, $-\text{OCH}_2\text{CH}_2-$), 1.86-1.80 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.50-1.43 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.41-1.21 (m, 32H, $-\text{CH}_2-$), 0.87 (t, $J = 6.4$ Hz, 6H) FT-IR (Nujol): 1733 cm^{-1} (C=O rings), 1697 cm^{-1} (C=O TIPS), 1251 cm^{-1} ($\text{C}_{\text{Ar}}\text{-O}$).

Compounds 7. 1 mmol of the corresponding triisopropyl protected compound, **6**, was dissolved in DCM and cooled down to $-78\text{ }^\circ\text{C}$ using $^i\text{PrOH}$ /liquid N_2 . The solution was stirred for 5 min. and then 5 mmol of TBAF (1.0 M solution in THF) was slowly added via syringe with vigorous stirring. Acetic acid was added to the reaction mixture after 2 h. and the stirring proceeded for 5 min. longer to ensure that all residual TBAF was quenched before the mixture was allowed to warm to room temperature. The reaction mixture was diluted with DCM and washed with water. The organic layer was evaporated and the crude product was purified by two recrystallizations, from methanol and from toluene. Yield = 70 % of a light-orange solid. R_f (silica gel, Hexanes/Ethyl acetate, 8:2) = 0.15.

7 (A(S)10*-E(S)10*): DSC: $159.8\text{ }^\circ\text{C}$, 29.7 kJ/mol . $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 8.34 (d, $J = 8.7$ Hz, 2H, Ar-*H*), 8.29 (d, $J = 9.3$ Hz, 2H, Ar-*H*), 8.16 (d, $J = 9.0$ Hz, 2H, Ar-*H*), 7.99 (d, $J = 8.7$ Hz, 2H, Ar-*H*), 7.97 (d, $J = 8.7$ Hz, 2H, Ar-*H*), 7.94 (dd, $J = 1.8$ Hz, $J = 2.1$ Hz, 1H, Ar-*H* central ring *o*-COOH), 7.92 (dd, $J = 1.8$ Hz, $J = 2.1$ Hz, 1H, Ar-*H* central ring *o*-

COOH), 7.52 (dd, $J = 2.1$ Hz, 1H, Ar-*H* central ring *p*-COOH), 7.39 (d, $J = 8.7$ Hz, 2H, Ar-*H*), 7.03 (d, $J = 9.0$ Hz, 2H, Ar-*H*), 6.99 (d, $J = 8.7$ Hz, 2H, Ar-*H*), 4.09 (m, 4H, -OCH₂CH₂-), 1.92-1.83 (m, 2H, -CH-(CH₃)₂), 1.76-1.60 (m, 4H, -OCH₂CH₂-), 1.58-1.50 (m, 2H, -CH₂-CH(CH₃)-CH₂-), 1.38-1.24 (m, 6H, -CH₂-), 1.22-1.11 (m, 6H, -CH₂-), 0.97 (d, $J = 6.3$ Hz, 3H, -CH(CH₃)-), 0.96 (d, $J = 6.3$ Hz, 3H, -CH(CH₃)-), 0.87 (d, $J = 6.6$ Hz, 12H, -CH(CH₃)₂). EA: calculated: C, 72.14; H, 6.95; N, 3.12; found: C, 72.07; H, 6.97; N, 3.26.

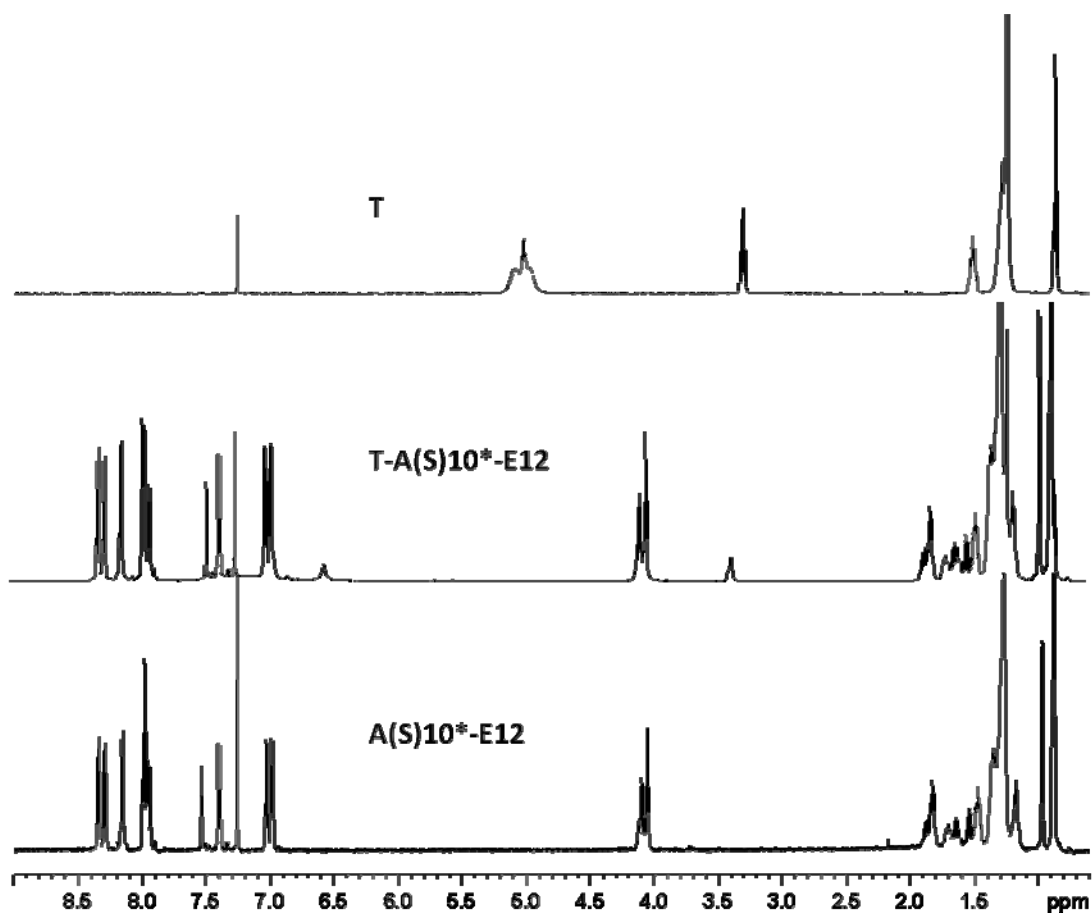
7 (A12-E(S)10*): DSC: 132.1 °C, 25.7 kJ/mol. ¹H-NMR (400 MHz, CDCl₃): δ 8.33 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.28 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 8.09 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 7.98 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.96 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.93 (dd, $J = 1.6$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *o*-COOH), 7.90 (dd, $J = 1.6$ Hz, $J = 2.4$ Hz, 1H, Ar-*H* central ring *o*-COOH), 7.51 (dd, $J = 2.0$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *p*-COOH), 7.39 (d, $J = 9.2$ Hz, 2H, Ar-*H*), 7.02 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 6.99 (d, $J = 8.8$ Hz, Ar-*H*), 4.08 (m, 4H, -OCH₂CH₂-), 1.92-1.80 (m, 3H, -CH-(CH₃)₂), -OCH₂CH₂CH₂-), 1.62-1.45 (m, 3H, -CH₂-CH(CH₃)-CH₂, -OCH₂CH₂CH₂CH₂-), 1.40-1.21 (m, 19H, -CH₂-), 1.20-1.12 (m, 3H, -CH₂-), 0.96 (d, $J = 6.8$ Hz, 3H, -CH(CH₃)₃), 0.90-0.85 (m, 9H, -CH(CH₃)₂-, -CH₂CH₂CH₃). FT-IR (Nujol): 3200-2300 cm⁻¹ (COO-H), 1735 cm⁻¹ (C=O rings), 1697 cm⁻¹ (C=O acid), 1253 cm⁻¹ (C_{Ar}-O). EA: calculated: C, 72.55; H, 7.18; N, 3.02; found: C, 72.48, H, 7.21, N, 3.01.

7 (A(S)10*-E12): DSC: 146.6 °C (33.0 kJ/mol). ¹H-NMR (400 MHz, CDCl₃): δ 8.34 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 8.33 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.14 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 7.98 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.96 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.93 (dd, $J = 1.6$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *o*-COOH), 7.90 (dd, $J = 1.6$ Hz, $J = 2.4$ Hz, 1H, Ar-*H* central ring *o*-COOH), 7.51 (dd, $J = 2.0$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *p*-COOH), 7.39 (d, $J = 9.2$ Hz, 2H, Ar-*H*), 7.02 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 6.99 (d, $J = 8.8$ Hz, Ar-*H*), 4.08 (m, 4H, -OCH₂CH₂-), 1.92-1.80 (m, 3H, -CH-(CH₃)₂), -OCH₂CH₂CH₂-), 1.62-1.45 (m, 3H, -CH₂-CH(CH₃)-CH₂, -OCH₂CH₂CH₂CH₂-), 1.40-1.21 (m, 19H, -CH₂-), 1.20-1.12 (m, 3H, -CH₂-), 0.96 (d, $J = 6.8$ Hz, 3H, -CH(CH₃)₃), 0.90-0.85 (m, 9H, -CH(CH₃)₂-, -CH₂CH₂CH₃). FT-IR (Nujol): 3200-2300 cm⁻¹ (COO-H), 1735 cm⁻¹ (C=O rings), 1697 cm⁻¹ (C=O acid), 1253 cm⁻¹ (C_{Ar}-O). EA: calculated: C, 72.55; H, 7.18; N, 3.02; found: C, 72.45, H, 7.25, N, 2.99.

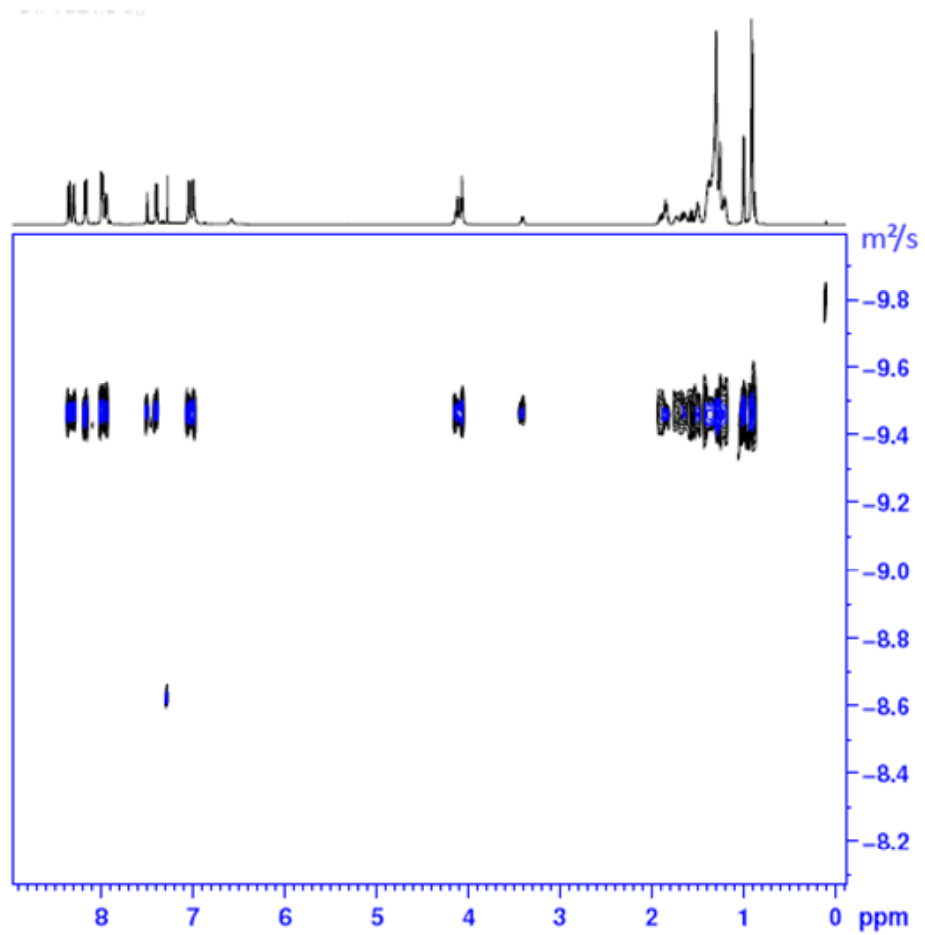
7 (A12-E12): DSC: 146.0 °C, 40 kJ/mol. ¹H-NMR (400 MHz, CDCl₃): δ 8.34 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.29 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 8.16 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 7.99 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.97 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 7.96 (d, $J = 8.4$ Hz, 2H, Ar-*H*), 7.93 (dd, $J = 1.6$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *o*-COOH), 7.90 (dd, $J = 1.6$ Hz, $J = 2.4$ Hz, 1H, Ar-*H* central ring *o*-COOH), 7.53 (dd, $J = 2.0$ Hz, $J = 2.0$ Hz, 1H, Ar-*H* central ring *p*-COOH), 7.40 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 7.02 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 6.99 (d, $J = 8.8$ Hz, Ar-*H*), 4.10-4.02 (m, 4H, -OCH₂CH₂-), 1.86-1.80 (m, 4H, -OCH₂CH₂CH₂-), 1.50-1.43 (m, 4H, -OCH₂CH₂CH₂-), 1.41-1.21 (m, 32H, -CH₂-), 0.88 (t, $J = 6.4$ Hz, 6H) FT-IR (Nujol): 1733 cm⁻¹ (C=O rings), 1697 cm⁻¹ (C=O acid), 1251 cm⁻¹ (C_{Ar}-O). EA: calculated C, 72.93; H, 7.39; N, 2.93; found: C, 72.73; H, 7.42; N, 3.00.

The complexes were obtained after slowly evaporating a CH₂Cl₂ solution of components **T** and **7** in a ratio 1:3, respectively, by shaking at room temperature. The mixture, once heated to the isotropic state, was used for further experiments.

¹H NMR Studies

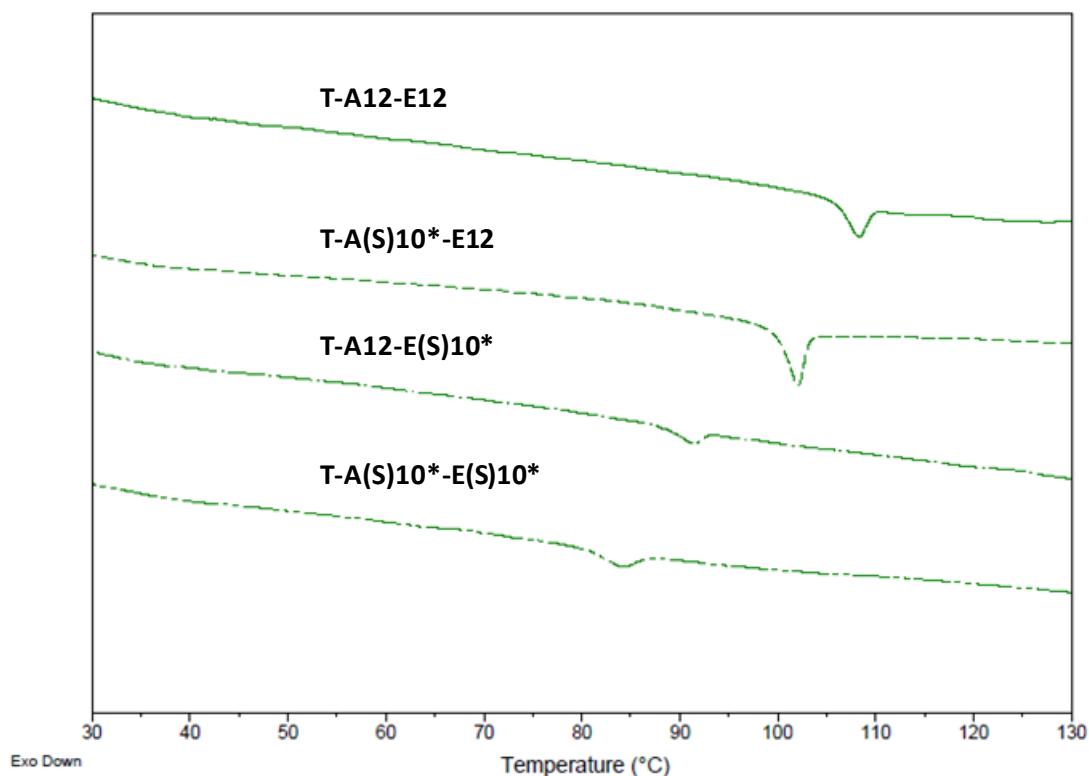


¹H NMR spectra in CDCl₃ of the triazine core, **T**, the complex, **T-A(S)10*-E12**, and the acid, **A(S)10*-E12**.



DOSY spectrum in CDCl_3 of the complex **T-A(S)10*-E12**.

DSC studies



Cooling thermograms recorded for all the complexes at a rate of 10 °C/min.

Density calculations:

The relationship between the density ρ of the complexes and the number Z of tetrameric complexes in the unit cell is given by the following equation:

$$\rho = \frac{M \cdot Z}{N \cdot V}$$

where M is the molar mass (in g) of each 1:3 complex, N the Avogadro number, and V the unit cell volume (in cm³). V is calculated by the formula

$$V_{\text{hex}} = \frac{\sqrt{3}}{2} \cdot a^2 \cdot h \cdot 10^{-24}$$

for a hexagonal lattice and

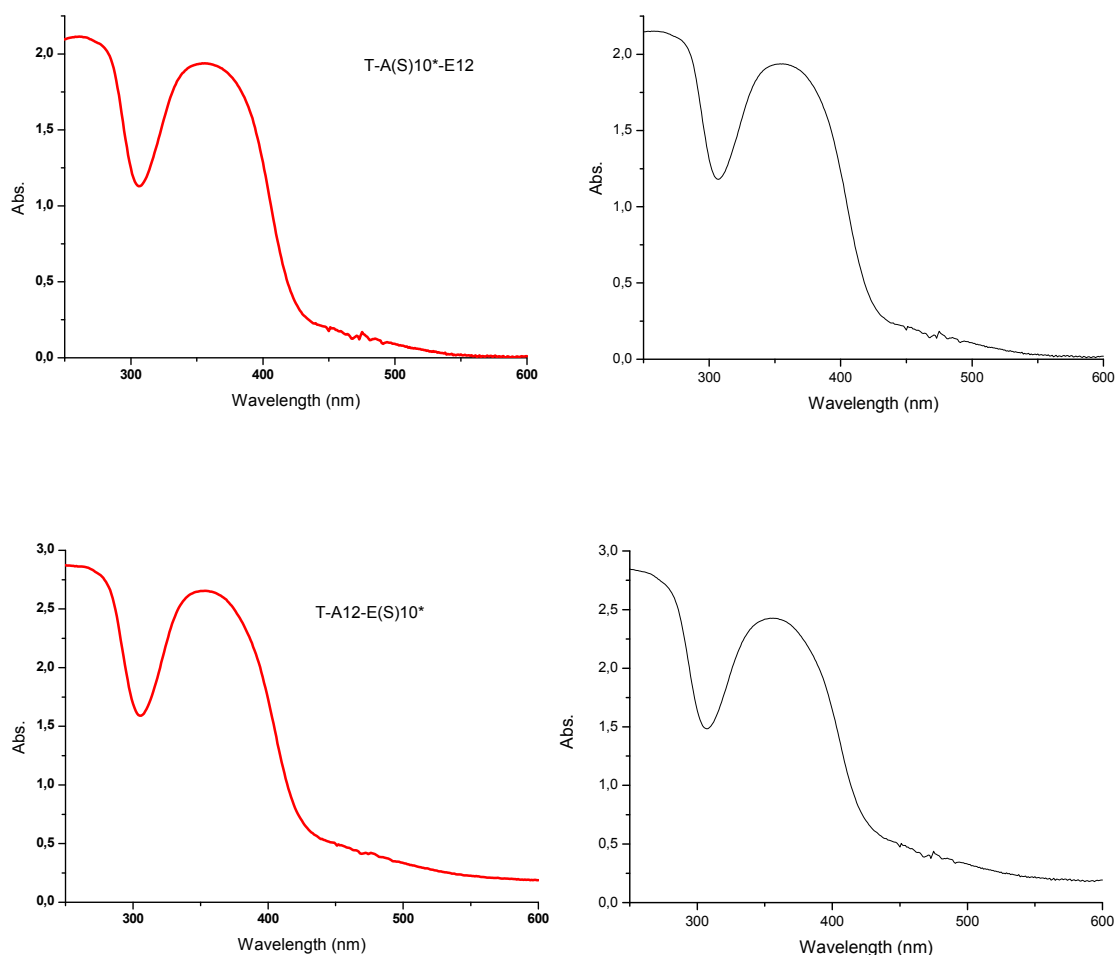
$$V_{\text{rec}} = a \cdot b \cdot h \cdot 10^{-24}$$

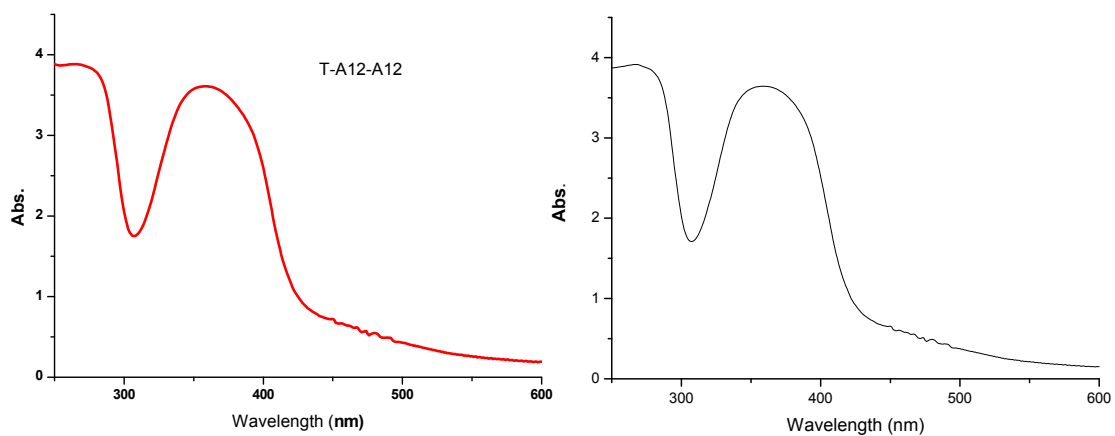
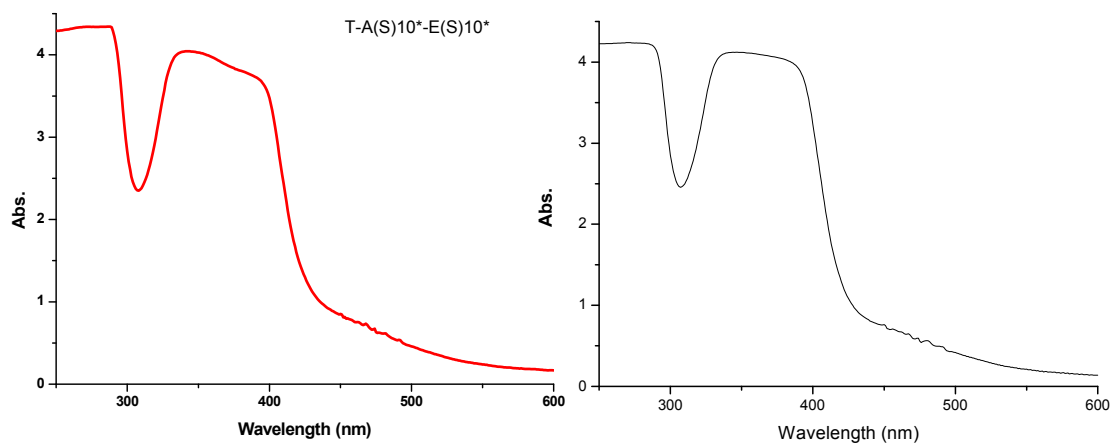
for an orthorhombic lattice, where a , b , h are the lattice constants in Å.

Thin film preparation and irradiation experiments.

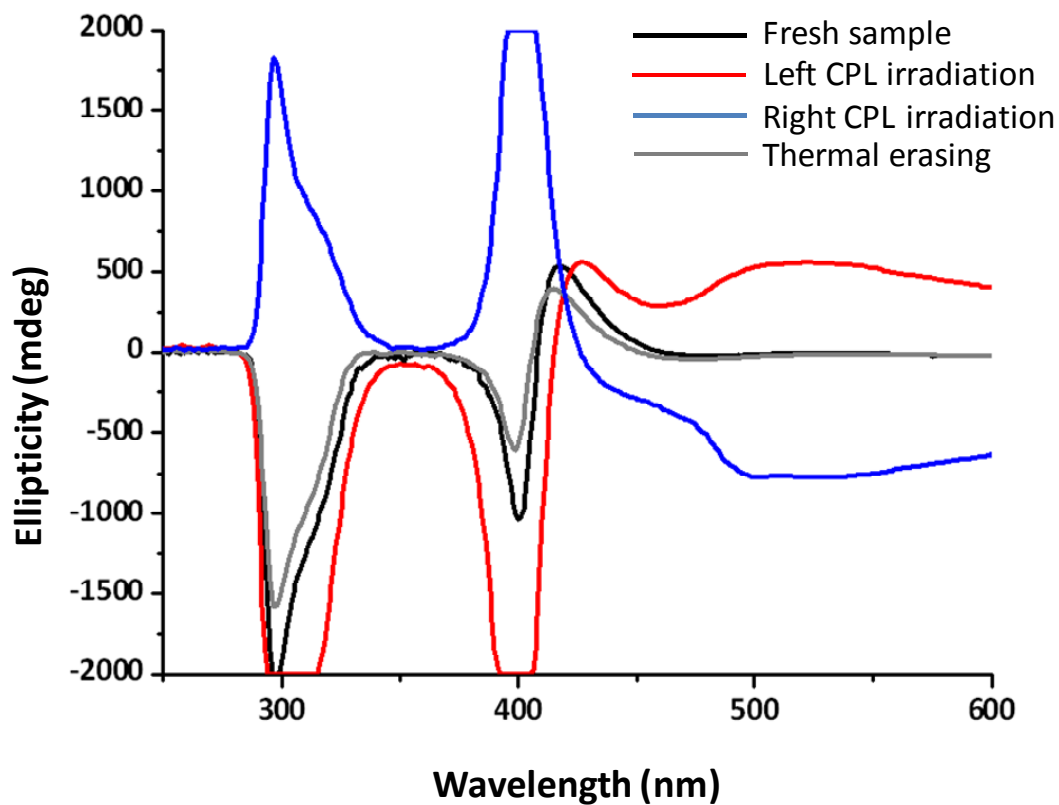
Thin films of the materials were prepared by casting solutions of the complexes in dichloromethane onto clean quartz plates. The films were dried under vacuum for 24 h. The films were then heated above the clearing temperature for 5 min and allowed to cool down room temperature at a rate of 10°C/min. The resulting films were irradiated for 30 minutes with the corresponding CPL from the 488 nm line of an Ar⁺ laser, power 20 mW cm⁻².

UV/Vis spectra recorded for the films before (red plot, left) and after (black plot, right) irradiation. For each compound, the UV-Vis profiles are similar before and after irradiation, and show a broad peak centered at ca. 350 nm that corresponds to the π - π^* transition of the *trans*-isomer of the azobenzene group, together with a maximum around 280 nm that corresponds to the phenyl benzoate group. Neither before nor after irradiation, a peak around 430 nm corresponding to the n - π^* transition – allowed for the nonplanar *cis* isomer of azobenzene – is not visible. This would indicate that the back isomerization of *cis* isomers to *trans* isomers is mostly complete for each material upon irradiation for 30 min.





**CD
studies**



Irradiation experiments and thermal erasing performed for a film of T- A (S) 10*-E(S)10*

General experimental details

NMR experiments were performed on a Bruker Avance 400 spectrometer, operating at frequency of 400.13 MHz for ^1H and 100.61 MHz for ^{13}C .

Infrared spectra for all the complexes were obtained by using a Mattson Genesis II FTIR spectrophotometer in the 400-4000 cm^{-1} spectral range.

Microanalyses were performed with a LECO CHNS-932 microanalyzer. IR spectra were recorded on a Thermo Nicolet Avatar 380 FTIR spectrophotometer between NaCl pellets. Mass spectra were obtained on MICROFLEX Bruker (MALDI+) spectrometer.

Mesophase analysis was performed using a Linkam THMS600 hot stage and an Olympus polarizing microscope BX51 equipped with an Olympus DP12 digital camera. Transition temperatures and enthalpies were obtained by differential scanning calorimetry with a DSC-MDSC Q-20 and Q-2000 from TA Instruments at heating and cooling rates of 10 $^{\circ}\text{C}/\text{min}$. The apparatus were previously calibrated with indium (156.6 $^{\circ}\text{C}$, 28.44 J/g).

Powder X-ray diffraction studies were carried out at room temperature using a Pinhole camera (Anton-Paar) operating with a point focused Ni-filtered $\text{Cu K}\alpha$ beam. The sample was held in Lindemann glass capillaries (1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The diffraction patterns were collected on a flat photographic film perpendicular to the x-ray beam.

X-ray diffraction studies of thin films were carried out at room temperature using a Reflection AD8-Advance diffractometer operating with a X-ray generator, with a 40 mm Göbel mirror and Ge (022) monochromator with a Cu beam anode and a platform for the rotation of the sample around the θ and χ axes.

Optical absorption spectra were recorded with a UV4-200 UV-Vis spectrophotometer from ATI Unicam.

CD spectra were recorded in a Jasco J-810. Neat samples were prepared by casting a solution of the material onto a quartz plate and subsequent melting above the clearing point. As heating stage, a Mettler FP82, with a central processor Mettler FP80, was used conveniently modified to fix within the sample holder of the CD spectrometer. Solution experiments were carried out in dichloromethane at room temperature.

AFM studies were performed with a Nanoscope IIIa, Veeco, Digital Instrument Inc. system. The images were taken at room temperature on the same films used for CD measurements.

SEM micrographs were taken on an Environmental Scanning Microscope Quanta FEG400, FEI.