# Combined reversible switching of ECD and quenching of CPL with chiral fluorescent macrocycles

## **Supporting Information**

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# 1. General Information and Materials

## 1.1. Synthesis and characterization

All reactions involving air sensitive compounds were carried out under  $N_2$  or argon by means of an inert gas/vacuum double manifold line and standard Schlenk techniques using dry solvents (CH<sub>2</sub>Cl<sub>2</sub>, tetrahydrofuran, tetrahydropyran, 1,4-dioxane and Et<sub>3</sub>N). Reactions involving oxygen sensitive reagents were performed using degassed solvents. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification (*e.g.* 2-amino-fluorene, 1-amino-pyrene, 3-nitro-1,8-naphthalic anhydride, perylene, *tert*-butyl acetyl chloride). *t*-BuOK was sublimed prior to use.

Analytical thin-layer chromatographies (TLC) were performed with Silicagel 60  $F_{254}$  aluminium sheets from Merck. Flash column chromatographies were performed with Silica SiliaFlash P60, 40-63  $\mu$ m (230-400 mesh) and Aluminium oxide (neutral, Brockmann I, 50-200  $\mu$ m, 60 Å).

NMR spectra were recorded on a Bruker AVANCE III HD-NanoBay 400 MHz spectrometer, equipped with a 5 mm CryoProbe Prodigy, or on a Bruker II 500 MHz spectrometer, equipped with a 5 mm Cryogenic DCH ( $^{1}H/^{13}C$ ) probe at 298 K.  $^{1}H$  NMR chemical shifts are given in ppm relative to Me<sub>4</sub>Si using solvent resonances as internal standards (CDCl<sub>3</sub>  $\delta$  = 7.26 ppm, DMSO-d<sub>6</sub>  $\delta$  = 2.50 ppm, CD<sub>2</sub>Cl<sub>2</sub> $\delta$ = 5.32 ppm). Data were reported as follows: chemical shift ( $\delta$ ) in ppm, multiplicity (s = singulet, d = doublet, t = triplet, dd = doublet of doublet, q = quartet and m = multiplet), coupling constant (Hz) and integration. <sup>13</sup>C-NMR chemicals shifts were given in ppm relative to Me<sub>4</sub>Si with solvent resonances used as internal standards (CDCl<sub>3</sub>  $\delta$  = 77.16 ppm, DMSO-d<sub>6</sub>  $\delta$  = 39.52 ppm, CD<sub>2</sub>Cl<sub>2</sub> $\delta$  = 53.84 ppm). IR spectra were recorded with a Perkin-Elmer 100 FT-IR spectrometer using a diamond ATR Golden Gate sampling and are reported in wave numbers (cm<sup>-1</sup>). Melting points (m.p.) were measured in open capillary tubes with a Büchi B-550 melting point apparatus and were uncorrected. Low resolution electrospray mass spectra (LR-ESI-MS) were obtained on an API 150EX (AB/MDS Sciex) spectrometer. High resolution mass spectra (HR-MS) were recorded on a QSTAR Pulsar (AB/MDS Sciex) spectrometer by the Department of Mass Spectroscopy at the University of Geneva. Optical rotations were measured in a thermostated (20 °C) 10 cm long microcell at 589 nm (Na lamp).

## 1.2. CSP-HPLC

Enantiomers of compounds **pyrene-18C6**, **pyrene-18C4**, **pyrene-16C4**, **perylene-18C6**, **perylene-18C6**, **perylene-18C4**, **fluorene-16C4** and **NMI-18C6** were resolved by chiral stationary phase HPLC on an Agilent 1260 Infinity II apparatus (quaternary pump, auto sampler, column thermostat and diode array detector) using a semi-preparative CHIRALPAK<sup>®</sup> IG column (250 x 10 mm, 5 mic). Mixtures of HPLC grade CH<sub>2</sub>Cl<sub>2</sub> and acetonitrile (with 0.1% diethylamine as additive) were used as mobile phase. Samples were injected as solutions in pure CH<sub>2</sub>Cl<sub>2</sub>.

#### 1.3. Optical properties

Optical properties were recorded in analytical grade solvents (CH<sub>2</sub>Cl<sub>2</sub>, acetonitrile). UV-Vis absorption spectra were recorded on a JASCO V-650 spectrophotometer at 20 °C. Electronic circular dichroism (ECD) spectra were recorded on a Jasco J-815 spectropolarimeter at 20 °C in a 1 cm-cuvette.

Fluorescence spectra were measured using a Varian Cary 50 Eclipse spectrophotometer. All fluorescence spectra were corrected for the wavelength-dependent sensitivity of the detection. Fluorescence quantum yields  $\phi$  were measured in diluted solutions (at least 5 different concentrations for each sample) with an optical density lower than 0.1 using the following equation:

$$\frac{\Phi_x}{\Phi_r} = \left(\frac{A_r(\lambda)}{A(x\lambda)}\right) \left(\frac{n_x^2}{n_r^2}\right) \left(\frac{D_x}{D_r}\right)$$

where A is the absorbance at the excitation wavelength ( $\lambda$ ), n the refractive index and D the integrated intensity. "r" and "x" stand for reference and sample respectively. The fluorescence quantum yields were measured in acetonitrile relative to phenanthrene ( $\phi$  = 12.5% in EtOH), anthracene ( $\phi$  = 27% in EtOH) or coumarine 153 ( $\phi$  = 38% in EtOH). Excitation of reference and sample compounds was performed at the same wavelength.

The circularly polarized luminescence (CPL) spectra were recorded with the home-made spectrofluoropolarimeter previously described,<sup>1</sup> the samples were excited with an UV (365 nm) LED, using a 90° geometry between excitation and detection.

 $Ba(ClO_4)_2$  and  $NaBAr_F$  salts used for titration experiments were purchased from commercial sources and used without purification.

# 2. Synthesis and characterization of organic compounds

## 2.1. Synthesis of anilines

3-Amino-perylene was synthesized in two steps from commercially available perylene using procedures adapted from the literature.<sup>2</sup>

3-Amino-NMI (NMI: *N*-propyl-1,8-naphthalene monoimide) was prepared according to a previously described procedure starting from commercially available 3-nitro-1,8-naphthalic anhydride.<sup>3</sup>

## 2.1.1. Synthesis of 3-nitro-perylene



To a solution of perylene (500 mg, 1.98 mmol) in ethyl acetate (30 mL) were added  $Ac_2O$  (0.51 mL, 5.4 mmol, 2.7 equiv) and  $Cu(NO_3)_2 \cdot 2.5H_2O$  (690 mg, 2.97 mmol, 1.5 equiv). The mixture was stirred at 25 °C for 15 hours. The conversion was followed by TLC analysis. After completion of the reaction,  $H_2O$  (30 mL) and  $CH_2Cl_2$  (30 mL) were added, the layers were separated and the aqueous layer was extracted with  $CH_2Cl_2$  (3 x 50 mL). The combined organic layers were washed with  $H_2O$  (3 x 30 mL), dried over

anhydrous  $Na_2SO_4$ , filtered and concentrated under vacuum. The residue was purified by column chromatography (SiO<sub>2</sub>, pentane/CH<sub>2</sub>Cl<sub>2</sub> gradient: 8:2, 7:3, 6:4) to yield 500 mg (1.68 mmol, 297.31 g/mol, 85%) of 3-nitro-perylene as a red solid.

Spectral data match those reported in the literature.<sup>2a</sup>

## 2.1.2. Synthesis of 3-amino-perylene



To a suspension of 3-nitro-perylene (480 mg, 1.61 mmol) in EtOH (6 mL) were added Pd/C (10% in weight, 171 mg, 0.161 mmol, 0.1 equiv) and hydrazine (9.7 mL, 1M in THF, 9.7 mmol, 6 equiv). The mixture was heated at 80 °C for 15 h, then cooled to room temperature, filtered through a pad of Celite<sup>®</sup> and concentrated under vacuum to yield 430 mg (1.61 mmol, 267.33 g/mol, quant.) of 3-amino-perylene as a bright orange solid.

Spectral data match those reported in the literature.<sup>2b</sup>

#### 2.2. Synthesis of monomeric amides

Neopentylcarboxamides, bearing only one fluorophore, were synthesized and used as monomeric references for the analyses and for comparison with the optical properties of macrocyclic compounds.

Pyrene monomer was used as a monomeric reference for pyrene-18C6, pyrene-18C4 and pyrene-16C4 compounds.

Perylene monomer was used as a monomeric reference for perylene-18C6, perylene-18C4 and perylene-16C4 compounds.

Fluorene monomer was used as a monomeric reference for fluorene-18C6, fluorene-18C4 and fluorene-16C4 compounds.

NMI monomer was used as a monomeric reference for NMI-18C6 derivative.

2.2.1. General procedure for the synthesis of monomeric amides



In a 10 mL flask under nitrogen atmosphere, dry  $CH_2Cl_2$  (0.1 M) and dry NEt<sub>3</sub> (3 equivalents) were added to 1 equivalent of the aromatic amine. The mixture was cooled down to 0 °C (ice bath) and *tert*-butyl acetyl chloride (2 equivalents) was added in one portion. The cooling bath was removed and the reaction was allowed to reach 25 °C on its own and stirred for an additional 3 hours. The conversion was followed by TLC analysis. After completion, the reaction was quenched by the addition of water and the mixture was extracted three times with  $CH_2Cl_2$ . The combined organic layers were dried over anhydrous  $Na_2SO_4$  and concentrated under vacuum. The pure monomeric amide was obtained after purification by column chromatography.

#### 2.2.2. Pyrene monomer



According to the general procedure, 43 mg (0.2 mmol) of 1-amino-pyrene, 56  $\mu$ L (54 mg, 0.4 mmol) of *tert*-butyl acetyl chloride, 84  $\mu$ L (61 mg, 0.6 mmol) of dry NEt<sub>3</sub> and 2 mL of dry CH<sub>2</sub>Cl<sub>2</sub> yielded 58 mg (0.18 mmol, 315.42 g/mol, 92%) of **pyrene monomer** as an off-white solid.

**Purification conditions**: Column eluent (SiO<sub>2</sub>): CH<sub>2</sub>Cl<sub>2</sub>/methanol gradient (99.5:0.5, 99:1, 98:2).

 $R_{f} = 0.8$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 98:2)

**m.p.**: 207 °C - 209 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.25 (s, 9H, -CH<sub>3</sub>), 2.48 (s, 2H, -CH<sub>2</sub>-), 7.71 (s, 1H, NH), 7.99 - 8.19 (m, 8H, aromatics), 8.41 (d, 1H, *J* = 8.2 Hz, aromatic).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 30.2 (3 -CH<sub>3</sub>), 31.6 (1 C), 51.8 (1 -CH<sub>2</sub>-), 120.3 (1 CH aromatic), 122.6 (1 CH aromatic), 123.6 (1 C aromatic), 124.9 (1 C aromatic), 125.2 (1 CH aromatic), 125.3 (1 CH aromatic), 125.3 (1 CH aromatic), 125.6 (1 CH aromatic), 127.0 (1 CH aromatic), 127.5 (1 CH aromatic), 128.1 (1 CH aromatic), 129.2 (1 C aromatic), 130.5 (1 C aromatic), 130.9 (1 C aromatic), 131.5 (1 C aromatic), 170.8 (1 C=0).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3283, 3034, 2950, 2866, 1650, 1598, 1555, 1521, 1485, 1393, 1364, 1340, 1307, 1271, 1236, 1108, 1040, 961, 913, 841, 822, 794, 755, 709.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>22</sub>H<sub>22</sub>NO 316.1696, observed 316.1697 (0.2 ppm).

#### 2.2.3. Perylene monomer



According to the general procedure, 27 mg (0.1 mmol) of 3-aminoperylene, 28  $\mu$ L (27 mg, 0.2 mmol) of *tert*-butyl acetyl chloride, 42  $\mu$ L (30 mg, 0.3 mmol) of dry NEt<sub>3</sub> and 2 mL of dry CH<sub>2</sub>Cl<sub>2</sub> yielded 31 mg (0.085 mmol, 365.48 g/mol, 85%) of **perylene monomer** as a yellow-orange solid.

**Purification conditions**: Column eluent (SiO<sub>2</sub>): CH<sub>2</sub>Cl<sub>2</sub>/methanol (98:2).

 $R_{f} = 0.4$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 98:2)

**m.p.**: 240 °C - 243 °C

<sup>1</sup>**H-NMR** (400 MHz, DMSO-*d*<sub>6</sub>): δ/ppm = 1.11 (s, 9H, -CH<sub>3</sub>), 2.39 (s, 2H, -CH<sub>2</sub>-), 7.53 - 7.57 (m, 2H, aromatics), 7.61 (t, 1H, *J* = 8.0 Hz, aromatic), 7.76 - 7.81 (m, 3H, aromatics), 7.95 (d, 1H, *J* = 8.8 Hz, aromatic), 8.32 (d, 1H, *J* = 7.4 Hz, aromatic), 8.37 (t, 2H, *J* = 8.3 Hz, aromatics), 8.41 (d, 1H, *J* = 7.0 Hz, aromatic), 9.81 (s, 1H, NH).

<sup>13</sup>C-NMR (126 MHz, DMSO- $d_6$ ): δ/ppm = 29.8 (3 -CH<sub>3</sub>), 31.0 (1 -CH<sub>2</sub>-), 49.1 (1 C), 120,5 (1 C aromatic), 120.7 (1 C aromatic), 120.9 (1 C aromatic), 121.0 (1 C aromatic), 122.5 (1 C aromatic), 122.7 (1 C aromatic),126.6 (1 C aromatic), 126.9 (1 C aromatic), 127.0 (1 C aromatic), 127.4 (1 C aromatic), 127.5 (1 C aromatic), 127.7 (1 C aromatic), 128.0 (1 C aromatic), 128.5 (1 C aromatic), 128.6 (1 C aromatic), 129.7 (1 C aromatic), 130.5 (1 C aromatic), 130.8 (1 C aromatic), 133.7 (1 C aromatic), 134.3 (1 C aromatic), 170.6 (1 C=0).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3279, 2957, 2876, 1651, 1535, 1526, 1391, 1366, 1340, 1270, 1260, 1195, 1150, 1051, 989, 834, 814, 767.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>26</sub>H<sub>24</sub>NO 366.1852, observed 366.1848 (-1.1 ppm).

#### 2.2.4. Fluorene monomer



According to the general procedure, 36 mg (0.2 mmol) of 2-amino-fluorene, 56  $\mu$ L (54 mg, 0.4 mmol) of *tert*-butyl acetyl chloride, 84  $\mu$ L (61 mg, 0.6 mmol) of dry NEt<sub>3</sub> and 2 mL of dry CH<sub>2</sub>Cl<sub>2</sub> yielded 56 mg (0.2 mmol, 279.38 g/mol, 99%) of **fluorene monomer** as an off-white solid.

**Purification conditions**: Column eluent (SiO<sub>2</sub>): CH<sub>2</sub>Cl<sub>2</sub>/methanol gradient (99:1, 98:2).

**R**<sub>f</sub> = 0.8 (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 98:2)

**m.p.**: 176 °C - 177 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.13 (s, 9H, -CH<sub>3</sub>), 2.25 (s, 2H, -CH<sub>2</sub>-), 3.89 (s, 2H, -CH<sub>2</sub>-), 7.12 (s, 1H, NH), 7.25 - 7.29 (m, 1H, aromatic), 7.32 (dd, 1H, J = 8.1 Hz, 2.0 Hz, aromatic), 7.36 (t, 1H, J = 7.5 Hz, aromatic), 7.52 (d, 1H, J = 7.5 Hz, aromatic), 7.70 (d, 1H, J = 8.1 Hz, aromatic), 7.72 (dd, 1H, J = 7.5 Hz, 2.0 Hz, aromatic), 7.72 (dd, 1H, J = 7.5 Hz, 2.0 Hz, aromatic), 7.93 (s, 1H, aromatic).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 30.0 (3 -CH<sub>3</sub>), 31.5 (1 C), 37.2 (1 -CH<sub>2</sub>-), 51.9 (1 -CH<sub>2</sub>-), 117.1 (1 CH aromatic), 118.7 (1 CH aromatic), 119.7 (1 CH aromatic), 120.2 (1 CH aromatic), 125.1 (1 CH aromatic), 126.4 (1 CH aromatic), 126.9 (1 CH aromatic), 136.8 (1 C aromatic), 138.2 (1 C aromatic), 141.5 (1 C aromatic), 143.3 (1 C aromatic), 144.5 (1 C aromatic), 170.2 (1 C=0).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3283, 2951, 2862, 1650, 1614, 1596, 1532, 1460, 1416, 1364, 1346, 1327, 1307, 1256, 1232, 1201, 1143, 1127, 876, 826, 710.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>19</sub>H<sub>22</sub>NO 280.1696, observed 280.1686 (-3.7 ppm).

#### 2.2.5. NMI monomer



According to the general procedure, 51 mg (0.2 mmol) of 3-amino-NMI, 56  $\mu$ L (54 mg, 0.4 mmol) of *tert*-butyl acetyl chloride, 84  $\mu$ L (61 mg, 0.6 mmol) of dry NEt<sub>3</sub> and 2 mL of dry CH<sub>2</sub>Cl<sub>2</sub> yielded 69 mg (0.2 mmol, 352.43 g/mol, 98%) of **NMI monomer** as an off-white solid.

**Purification conditions**: Column eluent (SiO<sub>2</sub>): CH<sub>2</sub>Cl<sub>2</sub>/methanol (99:1).

**R**<sub>f</sub> = 0.7 (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 98:2)

**m.p.**: 226 °C - 227 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.01 (t, 3H, J = 7.4 Hz, -CH<sub>3</sub>), 1.16 (s, 9H, -CH<sub>3</sub>), 1.72 - 1.79 (m, 2H, -CH<sub>2</sub>-), 2.34 (s, 2H, -CH<sub>2</sub>-), 4.12 - 4.15 (m, 2H, -CH<sub>2</sub>-), 7.42 (s, 1H, NH), 7.72 (dd, 1H, J = 8.2 Hz, 7.3 Hz, aromatic), 8.16 (dd, 1H, J = 8.2 Hz, 1.1 Hz, aromatic), 8.22 (d, 1H, J = 2.2 Hz, aromatic), 8.49 (dd, 1H, J = 7.3 Hz, 1.1 Hz, aromatic), 8.99 (d, 1H, J = 2.2 Hz, aromatic).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 11.7 (1 -CH<sub>3</sub>), 21.5 (1 -CH<sub>2</sub>-), 30.0 (3 -CH<sub>3</sub>), 31.7 (1 C), 42.2 (1 -CH<sub>2</sub>-), 51.9 (1 -CH<sub>2</sub>-), 122.4 (1 CH aromatic), 122.6 (1 C aromatic), 123.6 (1 C aromatic), 124.0 (1 CH aromatic), 125.3 (1 C aromatic), 127.7 (1 CH aromatic), 130.1 (1 CH aromatic), 132.8 (1 C aromatic), 133.9 (1 CH aromatic), 136.5 (1 C aromatic), 164.0 (1 C=O), 164.3 (1 C=O), 170.8 (1 C=O).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3247, 3072, 2965, 2870, 1699, 1653, 1627, 1596, 1534, 1503, 1463, 1423, 1376, 1338, 1271, 1235, 1124, 1072, 903, 782, 739, 706, 658.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for  $C_{21}H_{25}N_2O_3$  353.1860, observed 353.1855 (-1.3 ppm).

## 2.3. Synthesis of polyether macrocycles 16C4 and 18C4

Polyether macrocycle **18C6** was synthesized according to previously reported literature.<sup>4</sup> This procedure was adapted to the synthesis of macrocycles **16C4** and **18C4** (See Scheme S1 below).



Scheme S1. Synthesis of Unsaturated Macrocycles 18C6, 18C4 and 16C4

#### 2.3.1. Synthesis of polyether macrocycle 16C4



In a 5 mg vial, 1.42 mg (0.0007 mmol, 0.0001 equiv) of  $Rh_2(TCPTCC)_4$  was dissolved in 1.0 mL of dry THF. In a flame dried Schlenk, adapted with a condenser, under nitrogen atmosphere, was introduced the rhodium solution and the vial was washed with 0.7 mL of dry THF. Then, 10.0 mL of THF (for a total of 11.7 mL) were added, followed by

α-diazo-β-keto-methyl-ester **1** (1.00 g, 7 mmol, 1 equiv, c = 0.6 M). The solution was heated at 60 °C for 15 hours. The completion of the reaction was followed by TLC analysis and infrared spectroscopy (2146 cm<sup>-1</sup>). The solvent was removed under reduced pressure. The mixture was filtered through a pad of neutral alumina (solid deposit,<sup>5</sup> EtOAc/CH<sub>2</sub>Cl<sub>2</sub> 1:1) and the solvent was evaporated. The residual solid was dissolved in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> and 100 mL of pentane were added to precipitate the macrocycle. The macrocycle was filtered on a filtration funnel and washed with 100 mL of Et<sub>2</sub>O/pentane (1:9) to yield 338 mg (0.91 mmol, 372.41 g/mol, 26%) of **16C4** as a white solid.

 $R_{f} = 0.79$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 90:10)

**m.p.**: 129 °C - 132 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.78 - 1.84 (m, 4H, -CH<sub>2</sub>-), 1.89 - 1.95 (m, 4H, -CH<sub>2</sub>-), 2.38 (s, 6H, -CH<sub>3</sub>), 3.73 (t, 4H, *J* = 7.2 Hz, -CH<sub>2</sub>-), 3.75 (s, 6H, -CH<sub>3</sub>), 4.00 (t, 4H, *J* = 5.8 Hz, -CH<sub>2</sub>-).

<sup>13</sup>**C-NMR** (126 MHz, CDCl<sub>3</sub>): δ/ppm = 14.4 (2 -CH<sub>3</sub>), 26.2 (2 -CH<sub>2</sub>-), 26.8 (2 -CH<sub>2</sub>-), 51.5 (2 -CH<sub>3</sub>), 67.7 (2 -CH<sub>2</sub>-), 73.6 (2 -CH<sub>2</sub>-), 130.1 (2 =C), 158.7 (2 =C), 166.9 (2 C=O).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 2944, 2886, 1689, 1604, 1439, 1379, 1304, 1266, 1207, 1190, 1157, 1083, 1034, 1013, 972, 776, 631.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>18</sub>H<sub>29</sub>O<sub>8</sub> 373.1857, observed 373.1856 (-0.2 ppm).

#### *2.3.2.* Synthesis of polyether macrocycle **18C4**



In a 3 mL vial, 1.42 mg (0.0007 mmol, 0.0001 equiv) of  $Rh_2(TCPTCC)_4$  was dissolved in 1.0 mL of dry tetrahydropyran (THP). In a flame dried Schlenk, adapted with a condenser, under nitrogen atmosphere, was introduced the rhodium solution and the vial was washed with 0.7 mL of dry THP. Then, 10.0 mL of THP (for a total of

11.7 mL) were added, followed by  $\alpha$ -diazo- $\beta$ -keto-methyl-ester **1** (1.00 g, 7 mmol, 1 equiv, c = 0.6 M). The solution was heated at 60 °C for 15 hours. The completion of the reaction was followed by TLC analysis and infrared spectroscopy (2146 cm<sup>-1</sup>). The solvent was removed under reduced pressure. The residual solid was dissolved in 3 mL of CH<sub>2</sub>Cl<sub>2</sub> and 100 mL of pentane were added to precipitate the macrocycle. The macrocycle was filtered and washed with 100 mL of Et<sub>2</sub>O/pentane (1:9) to yield 771 mg (1.93 mmol, 400.47 g/mol, 55%) of **18C4** as a white solid.

 $R_{f} = 0.83$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 90:10)

**m.p.**: 95 °C - 96 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.65 - 1.76 (m, 12H, -CH<sub>2</sub>-), 2.36 (s, 6H, -CH<sub>3</sub>), 3.68 - 3.71 (m, 4H, -CH<sub>2</sub>-), 3.74 (s, 6H, -CH<sub>3</sub>), 3.99 - 4.01 (m, 4H, -CH<sub>2</sub>-).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 14.4 (2 -CH<sub>3</sub>), 23.4 (2 -CH<sub>2</sub>-), 29.8 (2 -CH<sub>2</sub>-), 30.1 (2 -CH<sub>2</sub>-), 51.5 (2 -CH<sub>3</sub>), 67.9 (2 -CH<sub>2</sub>-), 72.8 (2 -CH<sub>2</sub>-), 129.8 (2 =C), 158.7 (2 =C), 167.0 (2 C=O).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 2939, 1700, 1607, 1461, 1435, 1403, 1374, 1285, 1248, 1191, 1162, 1124, 1082, 1020, 1003, 971, 932, 885, 774, 732, 688, 620, 558.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>20</sub>H<sub>33</sub>O<sub>8</sub> 401.2170, observed 401.2176 (1.5 ppm).

## 2.4. Synthesis of functionalized macrocycles

## 2.4.1. General procedure for the synthesis of macrocycles

In a one neck flask under nitrogen atmosphere, dry tetrahydrofuran (c = 0.1 M) was added to 1 equivalent of polyether macrocycle (**18C6, 18C4** or **16C4**) and 3 equivalents of aromatic amine. The mixture was cooled down to -100 °C (EtOH/liquid nitrogen bath). Then 4 equivalents of freshly sublimed *t*-BuOK were added in one portion. After stirring for 1-2 minutes at -100 °C, the cooling bath was removed and the reaction was allowed to reach 25 °C on its own and stirred for an additional 3 hours. The conversion was followed by TLC analysis and LR-ESI-MS. Upon completion, the reaction was quenched by adding a few drops of methanol and directly purified by column chromatography (SiO<sub>2</sub>) without further treatment. A second column chromatography (Al<sub>2</sub>O<sub>3</sub>, neutral) could be required. Finally, the resulting oil or solid was purified by selective precipitation (dissolution in a minimal amount of  $CH_2Cl_2$  or ethyl acetate required for solubility, followed by addition of a large excess of pentane) affording the desired chiral polyether macrocycle.

**Pyrene-18C6**, **pyrene-18C4** and **pyrene-16C4** were synthesized according to the previously reported procedure.<sup>6</sup>

#### 2.4.2. Perylene-18C6



According to the general procedure, 100 mg (0.25 mmol) of **18C6**, 200 mg (0.75 mmol) of 3-amino-perylene, 2 mL of dry THF and 112 mg (1.0 mmol) of *t*-BuOK yielded 130 mg (0.15 mmol, 893.01 g/mol, 60%) of **perylene-18C6** (water adduct) as a yellow-orange solid.

Purification conditions:

Column eluent (SiO<sub>2</sub>):  $CH_2Cl_2$ , then  $CH_2Cl_2$ /methanol gradient (98:2, 95:5, 90:10).

Precipitation: CH<sub>2</sub>Cl<sub>2</sub> then pentane

 $\mathbf{R}_{f} = 0.3$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 95:5)

**m.p.**: 235 °C - 240 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 3.72 (m, 2H, -CH<sub>2</sub>-), 3.80 (m, 2H, -CH<sub>2</sub>-), 3.87 (m, 2H, -CH<sub>2</sub>-), 3.95 - 4.13 (m, 10H, -CH<sub>2</sub>-), 4.41 (d, 2H, J = 2.6 Hz, =CH<sub>2</sub>), 4.47 (s, 2H, -CH-), 4.52 (d, 2H, J = 2.6 Hz, =CH<sub>2</sub>), 7.04 - 7.11 (m, 6H, aromatics), 7.27 (d, 2H, J = 8.0 Hz, aromatics), 7.30 (d, 2H, J = 8.0 Hz, aromatics), 7.47 (d, 2H, J = 8.3 Hz, aromatics), 7.49 (d, 2H, J = 7.5 Hz, aromatics), 7.55 (d, 2H, J = 7.4 Hz, aromatics), 7.61 (d, 2H, J = 7.4 Hz, aromatics), 7.72 (d, 2H, J = 8.2 Hz, aromatics), 7.87 (d, 2H, J = 8.2 Hz, aromatics), 9.17 (s, 2H, NH).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 67.3 (2 -CH<sub>2</sub>-), 68.7 (2 -CH<sub>2</sub>-), 68.8 (2 -CH<sub>2</sub>-), 70.3 (2 -CH<sub>2</sub>-), 83.4 (2 -CH-), 89.7 (2 =CH<sub>2</sub>), 119.5 (4 CH aromatics), 119.6 (2 CH aromatics), 119.7 (2 CH aromatics), 119.9 (2 CH aromatics), 120.2 (2 CH aromatics), 126.0 (2 CH aromatics), 126.1 (2 CH aromatics), 126.3 (2 CH aromatics), 127.0 (2 CH aromatics), 127.1 (2 C aromatics), 127.5 (2 CH aromatics), 127.8 (2 C aromatics), 128.3 (2 C aromatics), 128.5 (2 C aromatics), 130.6 (4 C aromatics), 131.0 (2 C aromatics), 131.4 (2 C aromatics), 134.2 (2 C aromatics), 156.3 (2 =C), 167.2 (2 C=0).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3366, 2924, 2874, 1693, 1542, 1509, 1389, 1324, 1288, 1099, 996, 919, 807, 765, 731.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>56</sub>H<sub>47</sub>N<sub>2</sub>O<sub>8</sub> 875.3327, observed 875.3341 (1.6 ppm).

#### 2.4.3. Perylene-18C4



According to the general procedure, 50 mg (0.125 mmol) of **18C4**, 100 mg (0.375 mmol) of 3-amino-perylene, 1.5 mL of dry THF and 56 mg (0.5 mmol) of *t*-BuOK yielded 56 mg (0.064 mmol, 871.03 g/mol, 51%) of **perylene-18C4** as a yellow-brown solid.

Purification conditions:

Column 1 eluent (SiO<sub>2</sub>):  $CH_2Cl_2$ , then  $CH_2Cl_2$ /methanol gradient (99:1, 98:2, 96:4).

Column 2 eluent (SiO<sub>2</sub>):  $CH_2Cl_2$ , then  $CH_2Cl_2$ /methanol gradient (99.5:0.5, 99:1, 98:2).

Precipitation: CH<sub>2</sub>Cl<sub>2</sub> then pentane

**R**<sub>f</sub> = 0.4 (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 98:2)

**m.p.**: 246 °C - 248 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.54 (m, 2H, -CH<sub>2</sub>-), 1.76 (m, 2H, -CH<sub>2</sub>-), 1.84 (m, 2H, -CH<sub>2</sub>-), 1.97 - 2.07 (m, 4H, -CH<sub>2</sub>-), 2.40 (m, 2H, -CH<sub>2</sub>-), 3.62 - 3.74 (m, 6H, -CH<sub>2</sub>-), 4.02 (dt, 2H, J = 8.4 Hz, 3.8 Hz, -CH<sub>2</sub>-), 4.37 (d, 2H, J = 2.4 Hz, =CH<sub>2</sub>), 4.41 - 4.43 (m, 4H, -CH- and =CH<sub>2</sub>), 6.98 (d, 2H, J = 7.7 Hz, aromatics), 7.18 (d, 2H, J = 7.4 Hz, aromatics), 7.23 (m, 2H, aromatics), 7.30 - 7.33 (m, 4H, aromatics), 7.36 (d, 2H, J = 8.1 Hz, aromatics), 7.40 (d, 2H, J = 8.1 Hz, aromatics), 7.43 - 7.47 (m, 4H, aromatics), 7.64 (d, 2H, J = 7.3 Hz, aromatics), 7.81 (d, 2H, J = 7.4 Hz, aromatics), 8.37 (s, 2H, NH).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 25.2 (2 -CH<sub>2</sub>-), 29.8 (2 -CH<sub>2</sub>-), 31.2 (2 -CH<sub>2</sub>-), 68.5 (2 -CH<sub>2</sub>-), 68.6 (2 -CH<sub>2</sub>-), 83.3 (2 -CH-), 89.4 (2 -CH<sub>2</sub>-), 119.5 (2 CH aromatics), 119.7 (4 CH aromatics), 120.0 (2 CH aromatics), 120.2 (2 CH aromatics), 122.3 (2 CH aromatics), 126.0 (2 CH aromatics), 126.1 (2 CH aromatics), 126.2 (2 CH aromatics), 127.1 (2 CH aromatics), 127.75 (2 CH aromatics), 127.82 (2 C aromatics), 128.5 (2 C aromatics), 128.6 (2 C aromatics), 128.9 (2 C aromatics), 130.2 (2 C aromatics), 130.8 (2 C aromatics), 131.4 (2 C aromatics), 134.2 (2 C aromatics), 156.3 (2 =C), 167.5 (2 C=O).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3404, 2922, 2866, 1698, 1621, 1533, 1504, 1473, 1428, 1389, 1324, 1282, 1095, 1079, 1060, 994, 821, 806, 763.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for  $C_{58}H_{51}N_2O_6$  871.3742, observed 871.3758 (1.8 ppm).

#### 2.4.4. Perylene-16C4



According to the general procedure, 47 mg (0.125 mmol) of **16C4**, 100 mg (0.375 mmol) of 3-amino-perylene, 1.5 mL of dry THF and 56 mg (0.5 mmol) of *t*-BuOK yielded 55 mg (0.059 mmol, 927.92 g/mol, 47%) of **perylene-16C4** ( $CH_2Cl_2$  adduct) as a greenish-brown solid.

Purification conditions:

Column 1 eluent  $(SiO_2)$ :  $CH_2Cl_2$ , then  $CH_2Cl_2$ /methanol gradient (98:2, 95:5, 90:10).

Column 2 eluent (SiO<sub>2</sub>):  $CH_2Cl_2$ , then  $CH_2Cl_2$ /EtOAc gradient (98:2, 96:4, 94:6, 92:8).

Precipitation: CH<sub>2</sub>Cl<sub>2</sub> then pentane

**R**<sub>f</sub> = 0.4 (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 98:2)

**m.p.**: 249 °C - 250 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.79 - 1.90 (m, 4H, -CH<sub>2</sub>-), 2.06 - 2.17 (m, 4H, -CH<sub>2</sub>-), 3.64 (m, 2H, -CH<sub>2</sub>-), 3.70 - 3.74 (m, 4H, -CH<sub>2</sub>-), 3.93 (m, 2H, -CH<sub>2</sub>-), 4.42 (d, 2H, J = 2.4 Hz, =CH<sub>2</sub>), 4.46 (s, 2H, -CH-), 4.48 (d, 2H, J = 2.4 Hz, =CH<sub>2</sub>), 7.37 - 7.44 (m, 6H, aromatics), 7.60 - 7.67 (m, 6H, aromatics), 8.02 - 8.10 (m, 6H, aromatics), 8.15 (s, 4H, aromatics), 9.06 (s, 2H, NH).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 24.5 (2 -CH<sub>2</sub>-), 25.8 (2 -CH<sub>2</sub>-), 66.5 (2 -CH<sub>2</sub>-), 67.2 (2 -CH<sub>2</sub>-), 82.7 (2 -CH-), 89.7 (2 -CH<sub>2</sub>-), 119.8 (2 CH aromatics), 120.1 (2 CH aromatics), 120.2 (2 CH aromatics), 120.5 (4 CH aromatics), 120.6 (2 CH aromatics), 126.6 (2 CH aromatics), 126.8 (2 CH aromatics), 126.9 (2 CH aromatics), 127.6 (2 CH aromatics), 128.2 (2 CH + 2 C aromatics), 128.5 (2 C aromatics), 128.6 (2 C aromatics), 131.0 (2 C aromatics), 131.1 (2 C aromatics), 131.6 (2 C aromatics), 132.1 (2 C aromatics), 134.7 (2 C aromatics), 156.5 (2 =C), 167.2 (2 C=O).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3401, 3377, 3052, 2914, 2873, 1689, 1627, 1591, 1535, 1501, 1387, 1293, 1095, 1030, 952, 829, 808, 767, 728, 690.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>56</sub>H<sub>47</sub>N<sub>2</sub>O<sub>6</sub> 843.3429, observed 843.3423 (-0.6 ppm).

#### 2.4.5. Fluorene-18C6



According to the general procedure, 101 mg (0.25 mmol) of **18C6**, 136 mg (0.75 mmol) of 2-amino-fluorene, 2.5 mL of dry and degassed THF and 112 mg (1.00 mmol) of *t*-BuOK yielded 52 mg (0.07 mmol, 720.82 g/mol, 38%) of **fluorene-18C6** (water adduct) as a yellow solid.

Purification conditions:

Column eluent  $(SiO_2)$ :  $CH_2Cl_2$ /methanol gradient (100:0, 95:5, 90:10). Precipitation:  $CH_2Cl_2$ then pentane

 $\mathbf{R}_{f} = 0.5$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 9:1)

**m.p.**: 104 °C - 108 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 3.58 - 3.66 (m, 5H,  $-CH_2$ -), 3.67 - 3.76 (m, 5H,  $-CH_2$ -), 3.79 - 3.83 (m, 2H,  $-CH_2$ -), 3.87 - 3.96 (m, 6H,  $-CH_2$ -), 4.02 - 4.07 (m, 2H,  $-CH_2$ -), 4.33 (d, 2H, J = 2.7 Hz,  $=CH_2$ ), 4.39 (s, 2H, -CH-), 4.49 (d, 2H, J = 2.7 Hz,  $=CH_2$ ), 7.15 - 7.22 (m, 4H, aromatics), 7.34 - 7.36 (m, 2H, aromatics), 7.44 - 7.46 (m, 4H, aromatics), 7.50 - 7.52 (m, 2H, aromatics), 7.94 (s, 2H, aromatics), 9.52 (s, 2H, NH).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 37.1 (2 -CH<sub>2</sub>-), 66.9 (2 -CH<sub>2</sub>-), 68.7 (2 -CH<sub>2</sub>-), 69.2 (2 -CH<sub>2</sub>-), 70.2 (2 -CH<sub>2</sub>-), 83.4 (2 -CH-), 88.7 (2 =CH<sub>2</sub>), 116.6 (2 CH aromatics), 118.6 (2 CH aromatics), 119.5 (2 CH aromatics), 120.1 (2 CH aromatics), 124.9 (2 CH aromatics), 126.1 (2 CH aromatics), 126.7 (2 CH aromatics), 137.0 (2 C aromatics), 137.9 (2 C aromatics), 141.4 (2 C aromatics), 143.3 (2 C aromatics), 144.2 (2 C aromatics), 156.7 (2 =C), 167.3 (2 C=0).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3316, 2921, 1681, 1593, 1534, 1492, 1457, 1424, 1352, 1290, 1094, 1074, 993, 948, 827, 766, 732, 702, 573.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>42</sub>H<sub>43</sub>N<sub>2</sub>O<sub>8</sub> 703.3014, observed 703.3029 (2.1 ppm).

#### 2.4.6. Fluorene-18C4



According to the general procedure, 100 mg (0.25 mmol) of **18C4**, 136 mg (0.75 mmol) of 2-amino-fluorene, 2.5 mL of dry and degassed THF and 112 mg (1.00 mmol) of *t*-BuOK yielded 33 mg (0.05 mmol, 698.86 g/mol, 19%) of **fluorene-18C4** as a yellow solid.

Purification conditions:

Column eluent (SiO<sub>2</sub>): ethyl acetate (remaining aniline co-eluted with **fluorene-18C4**)

Precipitation: ethyl acetate then pentane (this step was repeated twice)

 $\mathbf{R}_{f} = 0.7$  (SiO<sub>2</sub>, ethyl acetate)

**m.p.**: 176 °C - 177 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.66 - 1.84 (m, 12H, -CH<sub>2</sub>-), 3.52 - 3.78 (m, 10H, -CH<sub>2</sub>-), 3.88 - 3.92 (m, 2H, -CH<sub>2</sub>-), 4.27 (s, 2H, -CH-), 4.33 (d, 2H, *J* = 2.4 Hz, =CH<sub>2</sub>), 4.36 (d, 2H, *J* = 2.4 Hz, =CH<sub>2</sub>), 7.21 - 7.26 (m, 4H, aromatics), 7.32 - 7.34 (m, 2H, aromatics), 7.40 - 7.42 (m, 2H, aromatics), 7.48 - 7.46 (m, 2H, aromatics), 7.51 - 7.53 (m, 2H, aromatics), 7.90 (s, 2H, aromatics), 8.53 (s, 2H, NH).

<sup>13</sup>**C-NMR** (126 MHz, CDCl<sub>3</sub>): δ/ppm = 24.4 (2 -CH<sub>2</sub>-), 28.8 (2 -CH<sub>2</sub>-), 30.0 (2 -CH<sub>2</sub>-), 37.1 (2 -CH<sub>2</sub>-), 68.2 (2 -CH<sub>2</sub>-), 69.7 (2 -CH<sub>2</sub>-), 82.9 (2 -CH-), 88.5 (2 -CH<sub>2</sub>-), 116.7 (2 CH aromatics), 118.5 (2 CH aromatics), 119.7 (2 CH aromatics), 120.3 (2 CH aromatics), 125.0 (2 CH aromatics), 126.4 (2 CH aromatics), 126.8 (2 CH aromatics), 136.3 (2 C aromatics), 138.2 (2 C aromatics), 141.3 (2 C aromatics), 143.3 (2 C aromatics), 156.9 (2 =C), 167.3 (2 C=O).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3386, 2921, 2870, 1693, 1637, 1590, 1524, 1492, 1459, 1424, 1298, 1217, 1089, 998, 1217, 1089, 998, 947, 823, 766, 733, 566.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>44</sub>H<sub>47</sub>N<sub>2</sub>O<sub>6</sub> 699.3429, observed 699.3439 (1.4 ppm).

#### 2.4.7. Fluorene-16C4



According to the general procedure, 93 mg (0.25 mmol) of **16C4**, 136 mg (0.75 mmol) of 2-amino-fluorene, 2.5 mL of dry and degassed THF and 112 mg (1.00 mmol) of *t*-BuOK yielded 59 mg (0.09 mmol, 670.81 g/mol, 35%) of **fluorene-16C4** as a yellow solid.

Purification conditions:

Column eluent  $(SiO_2)$ : ethyl acetate (remaining aniline co-eluted with **fluorene-16C4**)

Precipitation: ethyl acetate then pentane (this step was repeated twice)

R<sub>f</sub> = 0.6 (SiO<sub>2</sub>, ethyl acetate)

**m.p.**: 159 °C - 161 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 1.69 - 1.75 (m, 4H, -CH<sub>2</sub>-), 1.94 - 2.01 (m, 4H, -CH<sub>2</sub>-), 3.53 - 3.66 (m, 6H, -CH<sub>2</sub>-), 3.80 - 3.89 (m, 6H, -CH<sub>2</sub>-), 4.30 (s, 2H, -CH-), 4.35 (d, 2H, J = 2.4 Hz, =CH<sub>2</sub>), 4.39 (d, 2H, J = 2.4 Hz, =CH<sub>2</sub>), 7.26 - 7.29 (m, 2H, aromatics), 7.34 - 7.37 (m, 2H, aromatics), 7.47 - 7.53 (m, 4H, aromatics), 7.71 - 7.73 (m, 4H, aromatics), 7.98 (s, 2H, aromatics), 8.59 (s, 2H, NH).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 24.2 (2 -CH<sub>2</sub>-), 25.5 (2 -CH<sub>2</sub>-), 37.2 (2 -CH<sub>2</sub>-), 66.4 (2 -CH<sub>2</sub>-), 67.6 (2 -CH<sub>2</sub>-), 82.3 (2 -CH-), 89.3 (2 =CH<sub>2</sub>), 116.7 (2 CH aromatics), 118.6 (2 CH aromatics), 119.7 (2 CH aromatics), 120.2 (2 CH aromatics), 125.1 (2 CH aromatics), 126.5 (2 CH aromatics), 126.9 (2 CH aromatics), 136.4 (2 C aromatics), 138.3 (2 C aromatics), 141.5 (2 C aromatics), 143.3 (2 C aromatics), 144.5 (2 C aromatics), 156.6 (2 =C), 166.9 (2 C=O).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3362, 3048, 2888, 1685, 1620, 1591, 1529, 1492, 1458, 1425, 1351, 1290, 1211, 1093, 1037, 951, 815, 762, 724, 570.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>42</sub>H<sub>43</sub>N<sub>2</sub>O<sub>6</sub> 671.3116, observed 671.3116 (0.1 ppm).

#### 2.4.8. NMI-18C6



According to the general procedure, 101 mg (0.25 mmol) of **18C6**, 191 mg (0.75 mmol) of 3-amino-NMI, 2.5 mL of dry THF and 112 mg (1.00 mmol) of *t*-BuOK yielded 37 mg (0.043 mmol, 866.92 g/mol, 17%) of **NMI-18C6** (water adduct) as a yellow solid.

Purification conditions:

Column 1 eluent  $(SiO_2)$ :  $CH_2Cl_2$ , then  $CH_2Cl_2$ /methanol gradient (98:2, 95:5, 90:10).

Column 2 eluent ( $Al_2O_3$ , neutral):  $CH_2Cl_2$  for the packing of the column, then  $CH_2Cl_2$ /methanol gradient (99:1, 98:2, 97:3).

Preparative TLC (SiO<sub>2</sub>): CH<sub>2</sub>Cl<sub>2</sub>/methanol (95:5)

 $\mathbf{R}_{f} = 0.5$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/methanol 9:1)

**m.p.**: 213 °C - 218 °C

<sup>1</sup>**H-NMR** (500 MHz, CDCl<sub>3</sub>): δ/ppm = 0.92 (t, 6H, J = 7.4 Hz, -CH<sub>3</sub>), 1.54 - 1.62 (m, 4H, -CH<sub>2</sub>-), 3.64 - 3.69 (m, 4H, -CH<sub>2</sub>-), 3.73 - 3.77 (m, 2H, -CH<sub>2</sub>-), 3.82 - 3.98 (m, 8H, -CH<sub>2</sub>-), 4.04 - 4.07 (m, 2H, -CH<sub>2</sub>-), 4.13 - 4.23 (m, 4H, -CH<sub>2</sub>-), 4.40 (d, 2H, J = 2.8 Hz, =CH<sub>2</sub>), 4.41 (s, 2H, -CH-), 4.51 (d, 2H, J = 2.8 Hz, =CH<sub>2</sub>), 7.48 (dd, 2H, J = 8.3 Hz, 7.2 Hz, aromatics), 7.79 (dd, 2H, J = 8.3 Hz, 1.1 Hz, aromatics), 8.13 (d, 2H, J = 2.1 Hz, aromatics), 8.16 (dd, 2H, J = 7.2 Hz, 1.1 Hz, aromatics), 8.67 (d, 2H, J = 2.1 Hz, aromatics), 9.85 (s, 2H, NH).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ/ppm = 11.5 (2 -CH<sub>3</sub>), 21.2 (2 -CH<sub>2</sub>-), 41.8 (2 -CH<sub>2</sub>-), 65.7 (2 -CH<sub>2</sub>-), 68.7 (2 -CH<sub>2</sub>-), 69.0 (2 -CH<sub>2</sub>-), 69.1 (2 -CH<sub>2</sub>-), 83.1 (2 -CH-), 88.9 (2 =CH<sub>2</sub>), 121.4 (2 CH aromatics), 121.8 (2 C aromatics), 122.7 (2 C aromatics), 123.8 (2 CH aromatics), 124.4 (2 C aromatics), 126.9 (2 CH aromatics), 129.4 (2 CH aromatics), 131.9 (2 C aromatics), 133.2 (2 CH aromatics), 136.5 (2 C aromatics), 156.5 (2 C=), 163.0 (2 C=O), 163.6 (2 C=O), 168.0 (2 C=O).

**IR** (neat):  $\tilde{v}$ /cm<sup>-1</sup> 3315, 2926, 1691, 1658, 1592, 1537, 1463, 1427, 1377, 1336, 1293, 1233, 1130, 1090, 1073, 991, 926, 885, 930, 778, 737, 666.

**HR MS (ESI)**  $[M+H]^+ m/z$  calculated for C<sub>46</sub>H<sub>49</sub>N<sub>4</sub>O<sub>12</sub> 849.3342, observed 849.3340 (-0.2 ppm).

## 2.5. Monomeric amides NMR spectra

#### 2.5.1. Pyrene monomer



#### 2.5.2. Perylene monomer



#### 2.5.3. Fluorene monomer





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## 2.6. Polyether macrocycles 16C4 and 18C4 NMR spectra

## 2.6.1. Polyether macrocycles **16C4**



## *2.6.2.* Polyether macrocycles **18C4**



-: f1 (ppm) . 170 . 140 

## 2.7. Functionalized polyether macrocycles NMR spectra

#### 2.7.1. Perylene-18C6



#### 2.7.2. Perylene-18C4



#### 2.7.3. Perylene-16C4



#### 2.7.4. Fluorene-18C6



-: f1 (ppm) . 170 . 140 -70 

#### 2.7.5. Fluorene-18C4



f1 (ppm) 

#### 2.7.6. Fluorene-16C4



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#### 2.7.7. NMI-18C6



-: f1 (ppm) . 140 -70 

# 3. CSP-HPLC separation

## 3.1. General remarks

Compounds were resolved by chiral stationary phase HPLC using a semi-preparative CHIRALPAK<sup>®</sup> IG column. It is worth mentioning that it is necessary to remove traces of  $Et_2NH.HCl$  present in the separated compounds. The residue was thus dissolved in  $CH_2Cl_2$ , the organic phase was washed three times with  $H_2O$ , dried over anhydrous  $Na_2SO_4$ , filtered and concentrated under vacuum to afford the pure products.

## 3.2. Summary of separation data

The separation data are summarized in the following table:

		a	retention		
Entry	Compound	Mobile phase	1 <sup>st</sup> eluted	2 <sup>nd</sup> eluted	α
1	Pyrene-18C6	7:3	13.57	21.84	1.81
2	Pyrene-18C4	7:3	12.06	26.18	2.53
3	Pyrene-16C4	8:2 <sup>b</sup>	9.40	34.93	6.22
4	Perylene-18C6	9:1 <sup>b</sup>	13.36	51.37	5.32
5	Perylene-18C4	8:2 <sup>b</sup>	6.07	12.95	3.41
6	Perylene-16C4	8:2 <sup>b</sup>	9.97	55.46	7.71
7	Fluorene-18C6	7:3	11.12	24.17	2.69
8	Fluorene-18C4	7:3 <sup>b</sup>	7.55	16.07	3.80
9	Fluorene-16C4	7:3 <sup>b</sup>	8.92	26.56	4.99
10	NMI-18C6	9:1	8.64	14.12	2.05

Table S1. Enantiomer separations by CSP HPLC: mobile phase, retention times and  $\alpha$ 

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub>+0.1% Et<sub>2</sub>NH/CH<sub>3</sub>CN+0.1% Et<sub>2</sub>NH, flow = 2 mL/min, 20 °C; <sup>b</sup> flow = 3 mL/min.

 $\alpha$  is calculated using the following formula:  $\alpha = \frac{t_{r_2} - t_0}{t_{r_1} - t_0}$ where  $t_{r_1}/t_{r_2}$  are the retention time of the first and the second eluted enantiomer and  $t_0$  is the dead time.

The optical rotation of the enantiopure fractions are collected in the following table:

		First eluted enantiomer		Second eluted enantiomer	
Entry	Compound	concentration (g/mL)	$[\alpha]_D^{20}$	concentration (g/mL)	$[\alpha]_D^{20}$
1	Pyrene-18C6 <sup>a</sup>	8.74·10 <sup>-6</sup>	-400	6.03·10 <sup>-6</sup>	+365
2	Pyrene-18C4 <sup>b</sup>	$1.6 \cdot 10^{-4}$	-275	$1.2 \cdot 10^{-4}$	+223
3	Pyrene-16C4 <sup>b</sup>	$1.0 \cdot 10^{-4}$	-144	$1.3 \cdot 10^{-4}$	+112
4	Perylene-18C6 <sup>b</sup>	$2.5 \cdot 10^{-4}$	-184	$2.0 \cdot 10^{-4}$	+163
5	Perylene-18C4 <sup>c</sup>	4.50·10 <sup>-5</sup>	+133	3.47·10 <sup>-5</sup>	-98
6	Perylene-16C4 <sup>c</sup>	4.06·10 <sup>-6</sup>	+271	6.63·10 <sup>-6</sup>	-316
7	Fluorene-18C6 <sup>b</sup>	7.0·10 <sup>-5</sup>	-37	7.0·10 <sup>-5</sup>	+31
8	Fluorene-18C4 <sup>b</sup>	3.5·10 <sup>-4</sup>	-23	$2.5 \cdot 10^{-4}$	+20
9	Fluorene-16C4 <sup>b</sup>	$1.2 \cdot 10^{-4}$	+17	1.3·10 <sup>-4</sup>	-15
10	<b>NMI-18C6</b> <sup>a</sup>	$1.40 \cdot 10^{-4}$	-64	$1.02 \ 10^{-4}$	+43

**Table S2.** Optical rotation of enantiopure compounds

<sup>a</sup> in acetonitrile; <sup>b</sup> in CHCl<sub>3</sub>; <sup>c</sup> in CH<sub>2</sub>Cl<sub>2</sub>.

## 3.3. HPLC traces

For each compound, the data are reported as follows: separation conditions, analytical HPLC trace of the racemate, analytical HPLC trace of the first eluted enantiomer, analytical HPLC trace of the second eluted enantiomer and semi-preparative HPLC trace.
#### 3.3.1. Pyrene-18C6

**CSP-HPLC**: semi-preparative IG,  $CH_2Cl_2$  (+0.1%  $Et_2NH$ )/ $CH_3CN$  (+0.1%  $Et_2NH$ ) = 70:30, 2 mL/min, 20 °C, sample: 23 mg/1.5 mL of  $CH_2Cl_2$ , injection 500 µL.



 $\mathbf{1}^{st}$  enantiomer: vials 1 to 4 were collected

2<sup>nd</sup> enantiomer: vials 5 to 12 were collected

#### 3.3.2. Pyrene-18C4

**CSP-HPLC**: semi-preparative IG,  $CH_2Cl_2$  (+0.1%  $Et_2NH$ )/ $CH_3CN$  (+0.1%  $Et_2NH$ ) = 70:30, 2 mL/min, 20 °C, sample: 25 mg/1.5 mL of  $CH_2Cl_2$ , injection 500 µL.



1<sup>st</sup> enantiomer: vials 1 and 2 were collected 2<sup>nd</sup> enantiomer: vials 4 to 7 were collected

#### 3.3.3. Pyrene-16C4

**CSP-HPLC**: semi-preparative IG,  $CH_2Cl_2$  (+0.1%  $Et_2NH$ )/ $CH_3CN$  (+0.1%  $Et_2NH$ ) = 80:20, 3 mL/min, 20 °C, sample: 16 mg/1.0 mL of  $CH_2Cl_2$ , injection 500 µL.





#### 3.3.4. Perylene 18C6





1<sup>st</sup> enantiomer: vials 2 to 5 were collected 2<sup>nd</sup> enantiomer: vials 7 to 105 were collected

#### 3.3.5. Perylene-18C4

**CSP-HPLC**: semi-preparative IG,  $CH_2Cl_2$  (+0.1%  $Et_2NH$ )/ $CH_3CN$  (+0.1%  $Et_2NH$ ) = 80:20, 3 mL/min, 20 °C, sample: 5 mg/1.5 mL of  $CH_2Cl_2$ , injection 500  $\mu$ L.



 $1^{st}$  enantiomer: vials 3 to 5 were collected  $2^{nd}$  enantiomer: vials 9 to 12 were collected

#### 3.3.6. Perylene-16C4

**CSP-HPLC**: semi-preparative IG,  $CH_2Cl_2$  (+0.1%  $Et_2NH$ )/ $CH_3CN$  (+0.1%  $Et_2NH$ ) = 80:20, 3 mL/min, 20 °C, sample: 5 mg/1.5 mL of  $CH_2Cl_2$ , injection 500  $\mu$ L.



1<sup>st</sup> enantiomer: vials 3 to 5 were collected

 $2^{nd}$  enantiomer: vials 9 to 15 were collected

#### 3.3.7. Fluorene-18C6





1<sup>st</sup> enantiomer: vials 1 to 3 were collected

2<sup>nd</sup> enantiomer: vials 6 to 14 were collected

#### 3.3.8. Fluorene-18C4

**CSP-HPLC**: semi-preparative IG,  $CH_2Cl_2$  (+0.1%  $Et_2NH$ )/ $CH_3CN$  (+0.1%  $Et_2NH$ ) = 70:30, 3 mL/min, 20 °C, sample: 9 mg/0.5 mL of  $CH_2Cl_2$ , injection 250 µL.



2<sup>nd</sup> enantiomer: vials 8 and 9 were collected

#### 3.3.9. Fluorene-16C4

**CSP-HPLC**: semi-preparative IG,  $CH_2Cl_2$  (+0.1%  $Et_2NH$ )/ $CH_3CN$  (+0.1%  $Et_2NH$ ) = 70:30, 3 mL/min, 20 °C, sample: 12 mg/0.5 mL of  $CH_2Cl_2$ , injection 250 µL.



1<sup>st</sup> enantiomer: vials 1 to 4 were collected

2<sup>nd</sup> enantiomer: vials 6 to 11 were collected

#### 3.3.10, NMI-18C6

CSP-HPLC: semi-preparative IG, CH<sub>2</sub>Cl<sub>2</sub> (+0.1% Et<sub>2</sub>NH)/CH<sub>3</sub>CN (+0.1% Et<sub>2</sub>NH) = 90:10, 2 mL/min, 20 °C, sample: 20 mg/1.5 mL of  $CH_2Cl_2$ , injection 500  $\mu$ L.



2<sup>nd</sup> enantiomer: vials 6 to 11 were collected

# 4. Spectroscopic data

## 4.1. UV-Vis absorption and fluorescence spectra

#### 4.1.1. Procedure

In a typical experiment, UV-Vis absorbance and fluorescence spectra of a solution of interest compound (ca.  $10^{-5}$  M) in acetonitrile or CH<sub>2</sub>Cl<sub>2</sub> were recorded in a 1 cm cell. For the complexation experiments, an excess of Ba(ClO<sub>4</sub>)<sub>2</sub> or NaBAr<sub>F</sub> was added to the solution and the UV-Vis absorbance and fluorescence spectra were recorded again.

#### 4.1.2. Summary of the optical properties

	Compound	$\lambda_{\max}$ (nm)			ф	
Entry		absorption	(monomer) emission	excimer emission	Without M <sup>n+</sup>	With M <sup>n+</sup>
1	pyrene-monomer	341	387	-	24% <sup>b</sup>	-
2	pyrene-18C6	345	387	490	24% <sup>b</sup>	<1% <sup>b</sup>
3	pyrene-18C4	348	387	481	46% <sup>b</sup>	<1% <sup>b</sup>
4	pyrene-16C4	350	387	491	32% <sup>b</sup>	<1% <sup>b</sup>
5	perylene-monomer	443	472	-	77% <sup>d</sup>	-
6	perylene-18C6	446	470	543	10% <sup>d</sup>	62% <sup>d</sup>
7	perylene-18C4	446	470	536	19% <sup>d</sup>	59% <sup>d</sup>
8	perylene-16C4	446	470	tailed	16% <sup>d</sup>	50% <sup>d</sup>
9	fluorene-monomer	288	335	-	18% <sup>c</sup>	-
10	fluorene-18C6	318	-	337	2% <sup>c</sup>	-
11	fluorene-18C4	316	-	338	2% <sup>c</sup>	-
12	fluorene-16C4	316	-	336	2% <sup>c</sup>	-
13	NMI-monomer	338	420	-	17%	-
14	NMI-18C6	340	386	485	10% <sup>b</sup>	18% <sup>b</sup>

#### Table S3. Spectroscopic data without and with cation<sup>a</sup>

<sup>a</sup> Ba(ClO<sub>4</sub>)<sub>2</sub>/CH<sub>3</sub>CN system used for **18C6** derivatives, NaBAr<sub>F</sub>/CH<sub>2</sub>Cl<sub>2</sub> system used for **18C4** and **16C4** compounds; <sup>b</sup> Relative to anthracene ( $\phi$  = 27% in EtOH); <sup>c</sup> Relative to phenanthrene ( $\phi$  = 12.5% in EtOH); <sup>d</sup> Relative to coumarine 153 ( $\phi$  = 38% in EtOH).

4.1.3. Spectra of the monomeric amides without and with  $Ba(ClO_4)_2$ 



**Figure S1.** Absorption (continuous lines) and fluorescence (dotted lines) spectra of **pyrene monomer** in acetonitrile without (red) or with (blue) Ba(ClO<sub>4</sub>)<sub>2</sub> (2 equiv).



**Figure S2.** Absorption (continuous lines) and fluorescence (dotted lines) spectra of **perylene monomer** in acetonitrile without (red) or with (blue) Ba(ClO<sub>4</sub>)<sub>2</sub> (2 equiv).



**Figure S3.** Absorption (continuous lines) and fluorescence (dotted lines) spectra of **fluorene monomer** in acetonitrile without (red) or with (blue) Ba(ClO<sub>4</sub>)<sub>2</sub> (2 equiv).



**Figure S4.** Absorption (continuous lines) and fluorescence (dotted lines) spectra of **NMI monomer** in acetonitrile without (red) or with (blue) Ba(ClO<sub>4</sub>)<sub>2</sub> (2 equiv).

#### 4.1.4. Spectra of the macrocycles without and with cations



Figure S5. Absorption (continuous lines) and fluorescence (dotted lines) spectra of pyrene-18C6 in acetonitrile without (red) or with (blue) Ba(ClO<sub>4</sub>)<sub>2</sub> (2 equiv).



Figure S6. Absorption (continuous lines) and fluorescence (dotted lines) spectra of pyrene-18C4 in  $CH_2Cl_2$  without (red) or with (blue) NaBAr<sub>F</sub> (2 equiv).



Figure S7. Absorption (continuous lines) and fluorescence (dotted lines) spectra of pyrene-16C4 in  $CH_2Cl_2$ without (red) or with (blue) NaBAr<sub>F</sub> (2 equiv).



Figure S8. Absorption (continuous lines) and fluorescence (dotted lines) spectra of perylene-18C6 in acetonitrile without (red) or with (blue) Ba(ClO<sub>4</sub>)<sub>2</sub> (2 equiv).



Figure S9. Absorption (continuous lines) and fluorescence (dotted lines) spectra of perylene-18C4 in  $CH_2Cl_2$ without (red) or with (blue)  $NaBAr_F$  (2 equiv).



**Figure S10.** Absorption (continuous lines) and fluorescence (dotted lines) spectra of **perylene-16C4** in CH<sub>2</sub>Cl<sub>2</sub> without (red) or with (blue) NaBAr<sub>F</sub> (2 equiv).



**Figure S11.** Absorption (continuous lines) and fluorescence (dotted lines) spectra of **fluorene-18C6** in acetonitrile without (red) or with (blue) of Ba(ClO<sub>4</sub>)<sub>2</sub> (2 equiv).



Figure S12. Absorption (continuous lines) and fluorescence (dotted lines) spectra of fluorene-18C4 in  $CH_2Cl_2$  without (red) or with (blue) NaBAr<sub>F</sub> (2 equiv).



Figure S13. Absorption (continuous lines) and fluorescence (dotted lines) spectra of fluorene-16C4 in  $CH_2Cl_2$  without (red) or with (blue) NaBAr<sub>F</sub> (2 equiv).



**Figure S14.** Absorption (continuous lines) and fluorescence (dotted lines) spectra of **NMI-18C6** in acetonitrile without (red) or with (blue) of Ba(ClO<sub>4</sub>)<sub>2</sub> (2 equiv).

## 4.2. ECD spectra

## *4.2.1.* General procedure

In a typical experiment, the ECD spectrum of a solution of enantiopure compound (ca.  $10^{-5}$  M) in acetonitrile or CH<sub>2</sub>Cl<sub>2</sub> was recorded in a 1 cm cell. For the complexation experiments, 3.0 equivalents ( $10^{-3}$  M stock solutions) of NaBAr<sub>F</sub> in dichloromethane or Ba(ClO<sub>4</sub>)<sub>2</sub> in acetonitrile were added to the solution and the ECD spectrum was recorded again.

#### 4.2.2. ECD spectra without and with $NaBAr_F$



Figure S15. ECD spectra of pyrene-18C6 (A), perylene-18C6 (B), fluorene-18C6 (C) and NMI-18C6 (D)-in  $CH_2Cl_2$  without (red) or with (blue) NaBAr<sub>F</sub>.



Figure S16. ECD spectra of pyrene-18C4 (A), perylene-18C4 (B) and fluorene-18C4 (C) in  $CH_2Cl_2$  without (red) or with (blue)  $NaBAr_F$ .



Figure S17. ECD spectra of pyrene-16C4 (A), perylene-16C4 (B) and fluorene-16C4 (C) in  $CH_2Cl_2$  without (red) or with (blue)  $NaBAr_F$ .

#### 4.3. CPL spectra

#### *4.3.1.* General procedure

In a typical experiment, the CPL spectrum of a solution of enantiopure compound (ca.  $10^{-5}$  M) in acetonitrile or CH<sub>2</sub>Cl<sub>2</sub> was recorded in a 1 cm cell. For the complexation experiments, 3.0 equivalents ( $10^{-3}$  M stock solutions) of NaBAr<sub>F</sub> in dichloromethane were added to the solution and the CPL spectrum was recorded again.

#### 4.3.2. CPL spectra without and with NaBAr<sub>F</sub>



Figure S18. CPL spectra of pyrene-18C4 (A) and perylene-18C4 (B) in  $CH_2Cl_2$  without (red) and with (blue) NaBAr<sub>F</sub>.



Figure S19. CPL spectra of pyrene-16C4 (A) and perylene-16C4 (B) in  $CH_2Cl_2$  without (red) and with (blue) NaBAr<sub>F</sub>.

#### 4.4. Reversibility

#### 4.4.1. Procedure

In a typical experiment, ECD/fluorescence/CPL spectrum of a solution of enantiopure compound (ca.  $10^{-5}$  M) in CH<sub>2</sub>Cl<sub>2</sub> was recorded. For the complexation experiments, 2 equiv of NaBAr<sub>F</sub> from a  $10^{-3}$  M solution in CH<sub>2</sub>Cl<sub>2</sub> were added to the solution and the spectrum was recorded again. To switch back the system, 2 equiv of 18-Crown-6 from a  $10^{-3}$  M solution in CH<sub>2</sub>Cl<sub>2</sub> were added to the solution and the spectrum was recorded again. To suitch back the spectrum was recorded again. The procedure was repeated over several cycles.



4.4.2. ECD reversibility



**Figure S20.** Reversible ECD (A) and intensities at 345 nm (B) for the first eluted (–)-enantiomer of **pyrene-18C6** over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



**Figure S21.** Reversible ECD (A) and intensities at 342 nm (B) for the first eluted (–)-enantiomer of **pyrene-16C4** over 6 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



**Figure S22.** Reversible ECD (A) and intensities at 446 nm (B) for the first eluted (–)-enantiomer of **perylene-18C6** over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



**Figure S23.** Reversible ECD (A) and intensities at 446 nm (B) for the first eluted (+)-enantiomer of **perylene-18C4** over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



**Figure S24.** Reversible ECD (A) and intensities at 446 nm (B) for the first eluted (+)-enantiomer of **perylene-16C4** over 4 cycles of NaBAr<sub>F</sub>/18C6 additions (red/blue: without/with NaBAr<sub>F</sub>).



**Figure S25.** Reversible ECD (A) and intensities at 314 nm (B) for the first eluted (–)-enantiomer of **fluorene-18C6** over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



**Figure S26.** Reversible ECD (A) and intensities at 315 nm (B) for the first eluted (–)-enantiomer of **fluorene-18C4** over4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



**Figure S27.** Reversible ECD (A) and intensities at 316 nm (B) for the first eluted (+)-enantiomer of **fluorene-16C4** over 5 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



**Figure S28.** Reversible ECD (A) and intensities at 398 nm (B) for the first eluted (–)-enantiomer of **NMI-18C6** over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).





Figure S29. Reversible fluoresence (A) and intensities at 490 nm (B) for pyrene-18C6 over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



Figure S30. Reversible fluoresence (A) and intensities at 481 nm (B) for pyrene-18C4 over 7 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



Figure S31. Reversible fluoresence (A) and intensities at 491 nm (B) for pyrene-16C4 over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



Figure S32. Reversible fluoresence (A) and intensities at 338 nm (B) for fluorene-18C4 over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



Figure S33. Reversible fluoresence (A) and intensities at 336 nm (B) for fluorene-16C4 over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



CPL reversibility

4.4.4.



**Figure S34.** Reversible (normalized) CPL (A) and intensities at 490 nm (B) for the first eluted (–)-enantiomer of **pyrene-18C6** over 4 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).



**Figure S35.** Reversible (normalized) CPL (A) and intensities at 491 nm (B) for the first eluted (–)-enantiomer of **pyrene-16C4** over 2 cycles of NaBAr<sub>F</sub>/18-Crown-6 additions (red/blue: without/with NaBAr<sub>F</sub>).

# 5. Computational Section

# 5.1. General remarks

All calculations were run with Gaussian'09 and Gaussian'16 suites of programs using defaults grids and convergence criteria.<sup>7</sup> The input geometry of all compounds was built starting from the X-ray structure of **pyrene-18C6** with (*S*,*S*) configuration bound to one water molecule. The conformational space was explored by varying manually the macrocycle–C(=O) and *N*–aryl bonds, and optimizing the resulting structures with DFT at M06-2X-D3/def2-SVP level,<sup>8</sup> including the IEF-PCM implicit solvent model for dichloromethane.<sup>9</sup> All converged structures displayed a clear  $\pi$ -stacking interaction between the aromatic rings. TDDFT calculations were run with different combinations of functionals ( $\omega$ B97X-D, M06-2X, B3LYP, CAM-B3LYP), basis sets (def2-SVP, def2-TZVP) and environment description (in vacuo or with IEF-PCM solvent model for dichloromethane). The number of roots (excited states) varied from 50 to 80 depending on the specific compound. The calculated spectra shown in Figures S36 and S37 were obtained with M06-2X and CAM-B3LYP functionals, which yielded the best agreement with the experimental spectra. ECD plots were generated from Gaussian log files using the program SpecDis.<sup>10</sup> The plotting parameters were chosen on a best-fitting basis, and are listed in the caption of Figure S37.

#### 5.2. Calculation results



**Figure S36.** (A,B) Structures of (*S*,*S*)-**fluorene-18C6** optimized with DFT at the M06-2X-D3/def2-SVP/PCM level after rotation around the *N*-aryl and macrocycle–C(=O) bonds. A and B offer two different viewpoints of the same structures. The yellow double arrows depict the direction of the transition moments for the  $\pi$ - $\pi$ \* transition around 280 nm, and the signed curved arrows the chirality defined by the moments. (C) ECD spectra calculated for each structure at CAM-B3LYP/def2-SVP/PCM level. The horizontal and vertical ranges are 190-340 nm and -400-+400, respectively. Plotting parameters:  $\sigma$  = 0.3 eV, wavelength shift +15 nm.



**Figure S37.** Summary of ECD calculation results for the (*S*,*S*)-**18C6** series. Calculation levels and plotting parameters: **fluorene-18C6**, see Figure S36, scaling factor 10; **pyrene-18C6**, M06-2X/def2-TZVP,  $\sigma$  = 0.25 eV, shift +12 nm, scaling factor 10; **perylene-18C6**, CAM-B3LYP/def2-SVP,  $\sigma$  = 0.15 eV, shift +20 nm, scaling factor 10; **NMI-18C6**, CAM-B3LYP/def2-TZVP,  $\sigma$  = 0.3 eV, no shift or scaling. The yellow double arrows depict the direction of the naphthalene long axes of NMI chromophore. See text explanation.

Because of the structural complexity and flexibility of the **18C6**-based macrocycles, ECD calculations were mainly intended for investigating the dependence of ECD spectra on the key structural parameters of the macrocycles.

In Figure S36, four structures of (*S*,*S*)-**fluorene-18C6** are reported which were obtained upon rotation around the *N*-aryl and macrocycle–C(=O) bonds. All structures feature a pair of stacked fluorene rings with clear chirality defined by their long axes, i.e. the direction along which the main  $\pi$ - $\pi$ \* transition around 280 nm is polarized. Accordingly, the respective calculated ECD spectra display strong ECD couplets, whose sign depends on the chirality defined by the transition moments. It is apparent that the modification the reciprocal arrangement of the fluorene rings (i.e., exchanging the fluorene in the front with that in the back) causes a sign reversal in the ECD couplet. This rearrangement is caused by concerted rotations around the macrocycle–C(=O) bonds.

While differing in sign and intensity, the four spectra are similar to each other in overall shape and position of bands. The weighted average of the four spectra (obtained using computed internal energies) is shown in Figure S37 (left). It consists in a negative ECD couplet, which is in agreement with experimental spectrum for the 1<sup>st</sup> eluted enantiomer (Figure 4C in the main text). The vibrational fine structure in the experimental spectrum cannot be predicted at the current level of calculation, which does not include vibronic effects.

For **pyrene-** and **perylene-18C6** we investigated the impact of switching the ring position on the ECD spectra (Figure S37, two middle columns). For (*S*,*S*)-**perylene-18C6** the situation is similar to **fluorene-18C6**: exchanging the ring position from front to back causes a sign reversal in the ECD couplet, which is also accompanied by a strong intensity decrease. The overall ECD profile consists in a negative ECD couplet, as experimentally found for the 2<sup>nd</sup> eluted enantiomer. The situation for **pyrene-18C6** is more complicated because the two arrangements – obtained after the rings exchange their positions – are associated with very different ECD profiles. The structure attained from re-optimization of the X-ray geometry is associated with a negative ECD couplet; the second structure with exchanged ring positions is associated instead with a red-shifted positive couplet (Figure S37). If one assumes that the first conformation is dominant in solution, the combination of the two would yield an overall spectrum similar to that observed for the 2<sup>nd</sup> eluted enantiomer (Figure 4A, main text), namely a positive ECD band at 350 nm (mainly due to the major conformer), flanked by a long-wavelength weak negative band (due to the minor conformer).

Finally, for **NMI-18C6** the rotamerism around the *N*-aryl bond has a pronounced impact on the orientation of the transition moments, polarized either along the chromophore long or short axis (see yellow double arrows in Figure S37). Therefore, we focused our attention on this degree of conformational freedom without switching the reciprocal position of the rings. The two different arrangements (obtained upon 180°-rotation around the *N*-aryl bonds) display ECD spectra which are almost the mirror image of each other long wavelengths, while having consistent shape and sign at shorter wavelengths (Figure S37, right). Assuming a coexistence of both structures in solution, this would lead to a signal cancelation at long wavelengths, yielding a positive exciton couplet at short wavelengths. The overall result resembles the ECD measured for the 2<sup>nd</sup> eluted enantiomer (Figure 4D, main text).

# 6. Crystallographic Data

CCDC number	1045593			
Empirical formula	C48 H42 N2 O6			
Formula weight	742.83			
Temperature	180.05(10) K			
Wavelength	1.54184 Å			
Crystal system	Triclinic			
Space group	P-1			
Unit cell dimensions	a = 11.8363(4) Å	α= 108.968(3)°		
	b = 12.6884(4) Å	β= 104.837(3)°		
	c = 14.8869(5) Å	γ = 104.872(3)°		
Volume	1897.34(13) Å <sup>3</sup>			
Z	2			
Density (calculated)	1.300 Mg/m <sup>3</sup>			
Absorption coefficient	0.687 mm <sup>-1</sup>			
F(000)	784			
Crystal size	0.3412 x 0.1328 x 0.0883 mm <sup>3</sup>			
Theta range for data collection	3.381 to 72.598°.			
Index ranges	-14<=h<=12, -13<=k<=15, -18<=l<=15			
Reflections collected	12970			
Independent reflections	7288 [R(int) = 0.0177]			
Completeness to theta = 67.000°	99.8 %			
Absorption correction	Semi-empirical from equivalents			
Max. and min. transmission	1.00000 and 0.91638			
Refinement method	Full-matrix least-squares on F <sup>2</sup>			
Data / restraints / parameters	7288 / 0 / 513			
Goodness-of-fit on F <sup>2</sup>	1.023			
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0888			
R indices (all data)	R1 = 0.0450, wR2 = 0.0954			
Extinction coefficient	n/a			
Largest diff. peak and hole	0.187 and -0.183 e.Å <sup>-3</sup>			


Figure S38. View of the asymmetric unit. Displacement ellipsoids are depicted at 50 percent probability level.

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