Electronic Supplementary Information

Large phenyl-substituted acenes by cycloaddition reactions of the 2,6-naphthodiyne synthon

Diego Rodríguez-Lojo, Dolores Pérez,*, Diego Peña,*, Enrique Guitián
Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782-Santiago de Compostela, Spain
diego.pena@usc.es

SUPPORTING INFORMATION

CONTENTS

<table>
<thead>
<tr>
<th>CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Experimental details and spectroscopic data</td>
<td>S2</td>
</tr>
<tr>
<td>2. Absorption and emission spectra</td>
<td>S5</td>
</tr>
<tr>
<td>3. Voltammograms</td>
<td>S8</td>
</tr>
<tr>
<td>4. $^1$H and $^{13}$C NMR spectra</td>
<td>S11</td>
</tr>
</tbody>
</table>
1. Experimental details and spectroscopic data

General methods
All reactions were carried out under argon using oven-dried glassware. Solvents were dried by distillation from a drying agent: THF from Na/benzophenone; CH$_3$CN from CaH$_2$.

Thin layer chromatography (TLC) was performed on Merck silica gel 60 F$_{254}$; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh).

$^1$H and $^{13}$C NMR spectra were recorded at 250 and 63 MHz (Bruker DPX-250 instrument), 300 and 75 MHz (Varian Mercury-300 instrument) or 500 and 125 MHz (Varian Inova 500), respectively. MALDI-TOF spectra were determined on a Bruker Autoflex instrument.

Commercial reagents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc. and were used without further purification. The naphthodiynne precursor 4, and dienones 11 and 12 were prepared following a published procedure.

However, bistriflate 4 is commercially available (ABCR GmbH).

Synthesis of tetracene 10

A solution of tetrabutylammonium fluoride (TBAF, 0.62 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone 8 (237 mg, 0.612 mmol) and naphthodiynne precursor 4 (160 mg, 0.281 mmol) in THF (5.6 mL). The mixture was heated at 50 ºC under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO$_2$; 5:2 hexane/CH$_2$Cl$_2$) to isolate tetracene 10 (54 mg, 23%) as a yellow solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 8.29 (s, 4H), 7.31–7.23 (m, 16H), 7.21 (d, $J$ = 6.6 Hz, 4H), 6.87–6.80 (m, 20H) ppm.

Synthesis of hexacene 6

A solution of tetrabutylammonium fluoride (TBAF, 0.39 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone 11 (147 mg, 0.387 mmol) and naphthodiynne precursor 4 (100 mg, 0.176 mmol) in THF (3.6 mL). The mixture was heated at 50 ºC under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO$_2$; 3:1 hexane/toluene, under N$_2$) to isolate hexacene 6 (22 mg, 15%) as a violet solid. $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ = 8.95 (s, 4H), 8.00 (d, $J$ = 7.7 Hz, 4H), 7.60 (d, $J$ = 8.2 Hz, 4H), 7.51 (dd, $J$ = 6.4, 3.0 Hz, 8H).

7.09 (t, J = 7.1 Hz, 4H), 6.85 (t, J = 8.1 Hz, 4H) ppm. $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$) δ = 142.48 (4C), 136.17 (4C), 133.66 (8CH), 132.97 (4C), 132.45 (4C), 132.00 (4CH), 131.11 (2C), 130.26 (4C), 129.72 (8CH), 128.37 (4CH), 127.93 (4CH), 127.18 (4CH), 126.76 (4CH), 124.27 (4CH) ppm. MS (MALDI-TOF) for C$_{66}$H$_{40}$, calculated: 832.31, found 832.28.

Synthesis of octacene 7

A solution of tetrabutylammonium fluoride (TBAF, 0.56 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone 12 (228 mg, 0.561 mmol) and naphthodiyne precursor 4 (145 mg, 0.255 mmol) in THF (6.5 mL). The mixture was heated at 50 ºC under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO$_2$; 3:1 hexane/toluene, under N$_2$) to isolate octacene 7 (40 mg, 18%) as a violet solid. $^1$H NMR (500 MHz, CD$_2$D$_2$Cl$_4$) δ = 8.52 (s, 4H), 7.74 (s, 4H), 7.69 (d, J = 7.5 Hz, 4H), 7.62–7.37 (m, 24H), 7.17 (t, J = 7.8 Hz, 4H) ppm. $^{13}$C NMR (125 MHz, CD$_2$D$_2$Cl$_4$) δ = 142.15 (4C), 136.46 (4C), 132.91 (8CH), 131.56 (4C), 131.01 (4C), 130.90 (4C), 130.18 (2C), 129.53 (8CH), 129.48 (4CH), 129.22 (4C), 128.09 (4CH), 126.96 (4CH), 126.60 (4C), 126.49 (4CH), 126.40 (4CH), 125.26 (4CH) ppm. MS (MALDI-TOF) for C$_{70}$H$_{40}$, calculated: 880.31, found 880.23.

Synthesis of tetraphenylanthracene precursor 13

Finely powdered anhydrous CsF (55 mg, 0.359 mmol) was added over a solution of cyclopentadienone 8 (126 mg, 0.329 mmol) and naphthodiyne precursor 4 (170 mg, 0.299 mmol) in CH$_3$CN/CH$_2$Cl$_2$ (2:1, 9.0 mL). The mixture was heated at 50 ºC under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO$_2$; 3:1 hexane/CH$_2$Cl$_2$) to isolate triflate 13 (84 mg, 40%) as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ = 8.27 (s, 1H), 8.22 (s, 1H), 8.04 (s, 1H), 7.82 (s, 1H), 7.39–7.21 (m, 10H), 7.01–6.78 (m, 10H), 0.43 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 152.40 (C), 140.49 (2C), 139.91 (C), 139.59 (C), 139.52 (C), 139.44 (C), 139.03 (CH), 138.59 (C), 138.27 (C), 132.14 (C), 131.73 (C), 131.62 (CH), 131.57 (CH), 131.36 (CH), 129.65 (C), 128.06 (CH), 128.01 (CH), 127.03 (CH), 126.95 (CH), 126.88 (CH), 126.82 (CH), 126.42 (CH), 125.74 (CH), 116.24 (CH), -0.45 (3CH$_3$) ppm. MS (MALDI-TOF) for C$_{40}$H$_{31}$F$_3$O$_3$Si, calculated: 702.19, found 702.23.
Synthesis of pentacene 15

A solution of tetrabutylammonium fluoride (TBAF, 0.040 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone 11 (10 mg, 0.026 mmol) and triflate 13 (16 mg, 0.023 mmol) in THF (2.0 mL). The mixture was stirred at r.t. under argon for 16 h. Then, the solvent was evaporated under reduced pressure, the residue was redissolved in THF (5 mL) and MeOH (10 mL) was added. The solid was filtered and washed with MeOH (3 x 15 mL) to obtain pentacene 15 (8.1 mg, 42%) as a red solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 8.54 (s, 2H), 8.32 (s, 2H), 8.09 (d, $J$ = 8.1 Hz, 2H), 7.56 (m, 12H), 7.28 (m, 12H), 6.85 (m, 12H) ppm. MS (MALDI-TOF) for C$_{66}$H$_{42}$, calculated: 834.33, found 834.19.

Synthesis of hexacene 16

A solution of tetrabutylammonium fluoride (TBAF, 0.106 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone 12 (32 mg, 0.078 mmol) and triflate 13 (50 mg, 0.071 mmol) in THF (3.0 mL). The mixture was stirred at r.t. under argon for 16 h. Then, MeOH (10 mL) was added and the solid was filtered and washed with MeOH (3 x 15 mL) to obtain hexacene 16 (23 mg, 40%) as a pink solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 8.56 (s, 2H), 8.33 (s, 2H), 7.79 (s, 2H), 7.74 (d, $J$ = 7.5 Hz, 2H), 7.54 (m, 12H), 7.26 (m, 12H), 6.84 (m, 10H) ppm. MS (MALDI-TOF) for C$_{68}$H$_{42}$, calculated: 858.33, found 858.21.
2. Absorption and emission spectra

![Graph](image1)

Figure S1. Absorption (solid line) and emission (dashed line) spectra of 10 in CH₂Cl₂.

![Graph](image2)

Figure S2. Absorption (solid line) and emission (dashed line) spectra of 6 in CH₂Cl₂.
Figure S3. Absorption (solid line) and emission (dashed line) spectra of 7 in CH₂Cl₂.

Figure S4. Absorption (solid line) and emission (dashed line) spectra of 15 in CH₂Cl₂.
Figure S5. Absorption (solid line) and emission (dashed line) spectra of 16 in CH₂Cl₂.
3. Voltammograms

Figure S6. Cyclic voltammogram of 10 in CH₂Cl₂/0.1 M Bu₄NPF₆ using AgCl/Ag as reference electrode.

Figure S7. Cyclic voltammogram of 6 in CH₂Cl₂/0.1 M Bu₄NPF₆ using AgCl/Ag as reference electrode.
Figure S8. Cyclic voltammogram of 7 in CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$ using AgCl/Ag as reference electrode.

Figure S9. Cyclic voltammogram of 15 in CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$ using AgCl/Ag as reference electrode.
Figure S10. Cyclic voltammogram of 16 in CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$ using AgCl/Ag as reference electrode.
4. $^1$H and $^{13}$C NMR spectra