Modulation of band gap and p- versus n-semiconductor character of ADA dyes by core and acceptor group variation

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1. Synthesis of building blocks

Scheme 1 Synthesis of building blocks 5, 6, 7, 8, and 9b. i) 1. LDA, 0 °C, 3.5 h; 2. ZnCl₂, 0 °C, 45 min; 3. CuCl₂, –78 °C to RT, 18 h. ii) RNH₂ (rac), Pd₂(dba)₃, BINAP, NaO’Bu, toluene, 110 °C, 25 h. iii) 1. POCl₃, DMF, 130 °C, 12 h; 2. 1 M NaOH (aq.), DCM, RT, 2 h. iv) 1. BuLi, Et₂O, –78 °C, 1 h, then RT, 1 h. 2. 3-thiophenecarboxaldehyde (14), –78 °C, 30 min, then RT, 3 h; 3. BuLi, –78 °C, 40 min, then RT, 2 h; 4. I₂, Et₂O, –20 °C, RT, 13.5 h. v) PCC, DCM, RT, 22 h. vi) Cu, DMF, 120 °C, 4 h. vii) 1. hydrazine hydrate, OHCH₂CH₂OH, 100 °C, 1 h; 2. KOH, H₂O, 180 °C, 3 h. viii) 1. 1.05 eq. BuLi, THF, –78 °C, 1 h, then RT, 1 h; 2. 1.05 eq. RBr (rac), –78 °C, 30 min, then RT, 2 h; 3. 1.05 eq. BuLi, THF, –78 °C, 1 h, then RT, 1 h; 4. 1.05 eq. RBr (rac), –78 °C, 30 min, then RT, 2 h. ix) DMF, POCl₃, DCE, 90 °C, 2 d. x) RBr (rac), NaOH (aq.), TBAB, toluene, reflux, 16 h. xi) DMF, POCl₃, 100 °C, 16 h. xii) Br₂, CHCl₃, RT, 20 h. xiii) RBr (rac), NaO’Bu, THF, RT, 16 h. xiv) 1. BuLi, THF, –78 °C, 40 min; DMF, –78 °C, 1 h, then RT, 1 h. xv) malononitrile, NaOAc, EtOH, RT, 40 min.

R = ethylhexyl (rac)
The starting material for the preparation of both bithiophene-containing donor cores was 3-bromothiophene (11). The synthesis of dialdehyde 5 encompassed three steps.\textsuperscript{S1-S3} Initial oxidative aromatic coupling of 11 provided bithiophene 12,\textsuperscript{S1} which was submitted to Buchwald-Hartwig amination.\textsuperscript{S2} The reaction employing Pd\textsubscript{2}dba\textsubscript{3}, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), and NaO\textsubscript{t}Bu produced DTP 13 in 92%. The sequence of the reactions was closed by Vilsmeier-Haack formylation.\textsuperscript{S3} Building block 6 was readily obtained in a six-step synthesis. Bis(2-iodo-3-thienyl)methanol (15) was prepared according to the reported procedure\textsuperscript{S4} in one pot from bromide 11 by its lithiation, followed by the reaction with 3-thiophenecarboxaldehyde (14), subsequent dilitiation and final reaction with iodine. Further, crude product was oxidized by PCC to ketone 16, which was finally converted into 17 via intramolecular Ullman reaction in 44% overall yield of the three synthetic steps.\textsuperscript{S4} In the next, step 17 was reduced via Wolff-Kishner reaction to afford 18 in 87% yield.\textsuperscript{S4} Consecutive alkylation therof gave 19 in 97%. The synthesis was accomplished by Vilsmeier-Haack formylation that produced donor core CPDT 6 in 58% yield.\textsuperscript{S5}

The preparation of carbazole building block was straightforward. To obtain 21 from carbazole (20), we applied a phase-transfer catalysis (PTC) methodology using ethylhexyl bromide as an alkylation agent and tetrabutylammonium bromide (TBAB) as a PTC catalyst.\textsuperscript{S6} The following Vilsmeier-Haack formylation afforded compound 7 in a moderate yield. Likewise, compound 8 could be easily prepared starting from commercially available fluorene (22). Bromination\textsuperscript{S7} followed by alkylation\textsuperscript{S8} afforded compound 24, which was subsequently transformed into dialdhyde 8 by applying "BuLi and DMF. Acceptor 9b was prepared following the procedure by Robertson.\textsuperscript{S9}

**General**

All reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. Reagent grade solvents were distilled prior to use. Column chromatography was performed on silica (silica gel, 230-400 mesh). \textsuperscript{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature, unless otherwise noted, and calibrated to the residual solvent signals or TMS. J values are given in Hz. Carbazole (20), 2-ethylhexyl bromide, fluorene (22), 3-bromothiophene (11), 3-thiophenecarboxaldehyde (14), and 1,3-indandione (9a) were commercially available.
Compounds $^{12}$S$^1$, $^{13}$S$^2$, $^5$S$^3$, $^{15}$S$^4$, $^{16}$S$^4$, $^{17}$S$^4$, $^{18}$S$^4$, $^6$S$^5$, $^{23}$S$^7$, $^{24}$S$^8$, and $^{9b}$S$^9$ were prepared according to the literature procedures.

**Synthesis of compound 19.**

![Compound 19](image)

Compound 19 was synthesized by adopting the reported procedure.$^{S^4}$ A solution of compound 18 (1.65 g, 9.26 mmol) in THF (50 mL) was cooled to –78 °C under nitrogen. Then the following operations were conducted: a) nBuLi (2.5 M in hexane; 3.9 mL, 9.72 mmol) was added dropwise and the mixture was kept at –78 °C for 1 h, followed by 1 h at room temperature; b) the mixture was again cooled to –78 °C, 2-ethylhexyl bromide (1.74 mL, 9.72 mmol) was added and after 30 min the reaction was stirred at room temperature for 2 h. Next, steps a) and b) were repeated using the same amounts of reagents. Afterwards, the solution was extracted with diethyl ether, washed with water, brine, NH$_4$Cl (aq.) and dried over MgSO$_4$. The crude product was purified by column chromatography (silica, pentane) to obtain 19 (3.62 g, 97%) as a light yellow oil. Compound 19 was obtained as a mixture of stereoisomers. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.14 (d, $J = 4.9$ Hz, 2H), 6.99-6.94 (m, 2H), 2.00-1.75 (m, 4H), 1.44-1.17 (m, 2H), 1.07-0.83 (m, 16H), 0.83-0.69 (m, 6H), 0.64-0.54 (m, 8H). Analytical data are in accordance with the literature.$^{S^{10}}$

**Synthesis of compound 21.**

![Compound 21](image)

Compound 21 was synthesized by adopting the reported procedure.$^{S^{11}}$ To a solution of carbazole ($^{20}$, 1.197 g, 7.16 mmol) and tetrabutylammonium bromide (46 mg, 0.14 mmol) in toluene (12 mL) NaOH (50% w/w; 4.6 g, 57.3 mmol) was added. Next, 2-ethylhexyl bromide
(1.60 g, 8.30 mmol) was added dropwise at RT to the mixture and the reaction was continued for 16 h under reflux. Afterwards, the layers were separated. The organic solvent was evaporated in vacuo and the residue was dissolved in CH₂Cl₂, washed with water and dried over MgSO₄. After filtration solvent was removed under reduced pressure and the crude product was purified by Kugelrohr distillation to afford 21 (1.90 g, 95%) as a yellowish oil. 

\(^1\)H NMR (400 MHz, CDCl₃) δ 8.14-8.07 (m, 2H), 7.50-7.36 (m, 4H), 7.25-7.19 (m, 2H), 4.26-4.07 (m, 2H), 2.15-1.99 (m, 1H), 1.47-1.18 (m, 8H), 0.92 (t, \(J = 7.4\) Hz, 3H), 0.87 (t, \(J = 7.2\) Hz, 3H). Analytical data are in accordance with the literature.\(^{S12}\)

**Synthesis of compound 7.**

![Compound 7](image)

Compound 7 was prepared by adopting the reported procedure.\(^{S13}\) A Schlenk tube was charged with dimethylformamide (24.20 g, 331 mmol) and the solvent was cooled to 0 °C. Then phosphorus oxichloride (50.76 g, 331 mmol) was added dropwise and the solution was stirred at 0 °C for 1 h. Next, compound 21 (5.00 g, 17.89 mmol) was added and the reaction mixture was stirred at 100 °C for 16 h. After cooling to 0 °C, the mixture was neutralized by adding NaOH solution (1 M). The product was extracted with CH₂Cl₂, washed with water and dried over Na₂SO₄. Column chromatography (silica, EtOAc/hexane 1:9 to 2:9) afforded 7 (1.82 g, 30 %) as a colorless solid. \(^1\)H NMR (400 MHz, CDCl₃) δ 10.14 (s, 2H), 8.67 (dd, \(J = 1.6, 0.5\) Hz, 2H), 8.08 (dd, \(J = 8.6, 1.6\) Hz, 2H), 7.54 (d, \(J = 8.6\) Hz, 2H), 4.26 (d, \(J = 7.6\) Hz, 2H), 2.14-2.00 (m, 1H), 1.49-1.20 (m, 8H), 0.94 (t, \(J = 7.4\) Hz, 3H), 0.85 (t, \(J = 7.1\) Hz, 3H). Analytical data are in accordance with the literature.\(^{S3}\)
**Synthesis of compound 8.**

A dried flask was charged with dibromofluorene 23 (104 mg, 0.19 mmol). The vessel was purged with nitrogen and closed with a septum. Afterwards, anhydrous THF (0.79 mL) was added and the solution was cooled under nitrogen to −78 ºC. Next, BuLi (2.5 M in hexane; 0.23 mL, 0.58 mmol,) was added dropwise over 5 min and the mixture was stirred at −78 ºC for ca. 40 min, followed by addition of anhydrous DMF (50 µL, 0.65 mmol) in THF (85 µL). The reaction was stirred at this temperature for 1 h. Then, the cooling bath was removed and the stirring was continued for 1 h. Afterwards, the reaction was quenched with a saturated aqueous NH₄Cl, and extracted with Et₂O. The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and evaporated. A crude product was purified by column chromatography (silica, hexane/EtOAc 19:1) to give 8 (57 mg, 67%) as a colorless solid. Compound 8 was obtained as a mixture of stereoisomers. ¹H NMR (400 MHz, CDCl₃) δ 10.09 (s, 2H), 7.99-7.95 (m, 2H), 7.95-7.89 (m, 4H), 2.14-2.03 (m, 4H), 0.94-0.70 (m, 12H), 0.70-0.57 (m, 10H), 0.52-0.44 (m, 6H), 0.44-0.35 (m, 2H). Analytical data are in accordance with the literature.¹¹⁴

### 2. Absorption and photoluminescence

UV/vis measurements were performed using Lambda 950 or Lambda 35 (Perkin-Elmer). All spectra were measured in dichloromethane (spectrophotometric grade) from Merck (Hohenbrunn, Germany) at a concentration of about 10⁻⁵ M⁻¹. Fluorescence spectra were recorded on a QM-4/2003 (PTI) using the optical dilution method (OD < 0.05).¹¹⁵ Absolute fluorescence quantum yields were measured on the Hamamatsu instrument equipped with an integrating sphere. The photoluminescence quantum yields of 4% and 2% were determined for compounds 1a and 2a, respectively. For other compounds the emission was below 1% and could not be quantified with our instrument.
Fig. S1 Absorption (blue, cyan, purple, pink lines) and corresponding photoluminescence spectra (red lines) of dyes 1a, 1b, 2a, 2b, 3a, 3b, and 4a (UV/vis: CH₂Cl₂, ~10⁻⁵ M, 298 K; Photoluminescence: CH₂Cl₂, ~10⁻⁷ M, 298 K). Solid lines present the spectra of compounds with IND acceptors, whereas dotted lines correspond to the spectra of DCIND derivatives.

Fig. S2 UV/vis spectra of mono-substituted dyes 2aⁿ, 3aⁿ, 3bⁿ and 4aⁿ (CH₂Cl₂, ~10⁻⁵ M, 298 K). Solid lines present the spectra of compounds with IND acceptors, whereas a dotted line corresponds to the spectrum of a DCIND derivative.
Table S1 Optical properties of the mono-substituted dyes in CH$_2$Cl$_2$ ($c = 2 \cdot 10^{-5}$ M).

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{abs}$ $^a$ [nm]</th>
<th>$\varepsilon_{max}$$^b$ [$10^4$ M$^{-1}$ cm$^{-1}$]</th>
<th>$\mu_{eg}^2$$^c$ [D$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a$^m$</td>
<td>507</td>
<td>70.1</td>
<td>93</td>
</tr>
<tr>
<td>3a$^m$</td>
<td>442</td>
<td>37.9</td>
<td>53</td>
</tr>
<tr>
<td>3b$^m$</td>
<td>502</td>
<td>27.1</td>
<td>49</td>
</tr>
<tr>
<td>4a$^m$</td>
<td>403</td>
<td>45.4</td>
<td>70</td>
</tr>
</tbody>
</table>

$^a$ Absorption maximum. $^b$ Molar absorption coefficient. $^c$ Square transition dipole moments calculated from the measured data.

3. Electrochemistry

Details regarding the CV measurements are given in the main text.

![Cyclic voltammograms](image)

Fig. S3 Cyclic voltammograms of 1a, 1b, 2a, 2b, 3a, 3b, and 4a (CH$_2$Cl$_2$, $\sim$10$^{-4}$ – 10$^{-5}$ M, 298 K; scan rate: 100 mV s$^{-1}$; supporting electrolyte: Bu$_4$NPF$_6$ (0.1 M); calibrated vs. Fc/Fc$^+$ as an internal standard). Solid lines present voltammograms of compounds with IND acceptors, whereas dotted lines correspond to the voltammograms of DCIND derivatives.
4. Calculation of HOMO, LUMO and band gaps

The HOMO/LUMO energy levels were calculated according to the following equations:

\[ E_{\text{HOMO}} = -e \left( E_{1/2}^{\text{ox}} - 5.15 \text{ eV} \right) \]
\[ E_{\text{LUMO}} = E_{\text{HOMO}} + \left( \frac{hc}{\lambda_{\text{max}}} \right) \]

The optical band gaps were calculated using the equation: \( E_{\text{g opt}} = E_{\text{HOMO}} - E_{\text{LUMO}} = \frac{hc}{\lambda_{\text{max}}} \).

The electrochemical band gaps were calculated with \( E_{\text{g CV}} = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} \). The deviation between electrochemical and the optical band gap is at about ± 0.1 eV.

Table S2 Optical and electrochemical properties of investigated ADA systems.

<table>
<thead>
<tr>
<th>Dye</th>
<th>( E_{1/2}^{\text{red}} ) [V]</th>
<th>( E_{1/2}^{\text{ox}} ) [V]</th>
<th>( \lambda_{\text{max}} ) [nm]</th>
<th>( E_{\text{HOMO}} ) [eV]</th>
<th>( E_{\text{LUMO}} ) [eV]</th>
<th>( E_{\text{g opt}} ) [eV]</th>
<th>( E_{\text{g CV}} ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-1.52 ( ^g )</td>
<td>+0.49</td>
<td>582</td>
<td>-5.64</td>
<td>-3.51</td>
<td>2.13</td>
<td>2.01</td>
</tr>
<tr>
<td>1b</td>
<td>-0.96 ( ^g )</td>
<td>+0.83 ( ^g )</td>
<td>665</td>
<td>-5.98</td>
<td>-4.12</td>
<td>1.86</td>
<td>1.79</td>
</tr>
<tr>
<td>2a</td>
<td>-1.30</td>
<td>+0.84</td>
<td>584</td>
<td>-5.99</td>
<td>-3.87</td>
<td>2.12</td>
<td>2.14</td>
</tr>
<tr>
<td>2b</td>
<td>-0.84 ( ^g )</td>
<td>+1.08</td>
<td>664</td>
<td>-6.23</td>
<td>-4.36</td>
<td>1.87</td>
<td>1.92</td>
</tr>
<tr>
<td>3a</td>
<td>-1.76 ( ^g )</td>
<td>+0.97 ( ^g )</td>
<td>478</td>
<td>-6.12</td>
<td>-3.53</td>
<td>2.59</td>
<td>2.73</td>
</tr>
<tr>
<td>3b</td>
<td>-1.25 ( ^g )</td>
<td>+0.93</td>
<td>542</td>
<td>-6.08</td>
<td>-3.79</td>
<td>2.29</td>
<td>2.18</td>
</tr>
<tr>
<td>4a</td>
<td>-1.51 ( ^g )</td>
<td>+1.26 ( ^g )</td>
<td>466</td>
<td>-6.41</td>
<td>-3.75</td>
<td>2.66</td>
<td>2.77</td>
</tr>
</tbody>
</table>

\( ^a \) Redox potentials vs. Fc/Fc\(^+\) in CH\(_2\)Cl\(_2\) (c \sim 10^{-4} – 10^{-5} \text{ M}); \text{ scan rate: 100 mV s}^{-1}; \text{ supporting electrolyte: Bu}_4\text{NPF}_6 (0.1 \text{ M}). \( ^b \) Absorption maximum. \( ^c \) \( E_{\text{HOMO}} = -e \left( E_{1/2}^{\text{ox}} - 5.15 \text{ eV} \right) \). \( ^d \) \( E_{\text{LUMO}} = E_{\text{HOMO}} + \left( \frac{hc}{\lambda_{\text{max}}} \right) \). \( ^e \) \( E_{\text{g opt}} = E_{\text{HOMO}} - E_{\text{LUMO}} \). \( ^f \) \( E_{\text{g CV}} = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} \). \( ^g \) Peak potential.

5. DFT calculations

DFT calculations were performed for a simplified model compound of 1a, 1b, 2a, 2b, 3a, 3b, 4a, and 4b (ethylhexyl chains were replaced by methyl groups) by using the Gaussian 09 program package\(^{16}\) with B3-LYP\(^{17}\) as a functional and def2-SVP\(^{18}\) as a basis set. The structures were geometry optimized, followed by frequency calculations on the optimized structures which confirmed the existence of a minimum.
Fig. S4 Geometry optimized structures (with B3LYP/def2-SVP) as well as orbital contour plots of HOMO and LUMO for model compounds of a) 1a, b) 1b, c) 3a, d) 3b, e) 4a, and f) 4b (ethylhexyl substituents replaced with methyl groups).

<table>
<thead>
<tr>
<th>Dye</th>
<th>$E_{\text{HOMO}}$ [eV]</th>
<th>$E_{\text{LUMO}}$ [eV]</th>
<th>$E_g$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-5.75</td>
<td>-3.21</td>
<td>2.54</td>
</tr>
<tr>
<td>1b</td>
<td>-6.07</td>
<td>-3.84</td>
<td>2.23</td>
</tr>
<tr>
<td>2a</td>
<td>-5.79</td>
<td>-3.29</td>
<td>2.50</td>
</tr>
<tr>
<td>2b</td>
<td>-6.10</td>
<td>-3.89</td>
<td>2.21</td>
</tr>
<tr>
<td>3a</td>
<td>-6.02</td>
<td>-2.78</td>
<td>3.24</td>
</tr>
<tr>
<td>3b</td>
<td>-6.25</td>
<td>-3.39</td>
<td>2.86</td>
</tr>
<tr>
<td>4a</td>
<td>-6.19</td>
<td>-3.15</td>
<td>3.04</td>
</tr>
<tr>
<td>4b $^a$</td>
<td>-6.44</td>
<td>-3.74</td>
<td>2.70</td>
</tr>
</tbody>
</table>

$^a$ Compound could not be isolated.
6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were carried out under nitrogen atmosphere using DSC Q1000 (TA Instruments) at a heating rate/cooling rate of 10 K min\(^{-1}\). At least two heating-cooling cycles were measured.

Fig. S5 DSC curves (heating and cooling) for molecules with IN acceptors (left) and with DCNIO acceptors (right) (heating rate/cooling rate 10 K min\(^{-1}\), N\(_2\)).

Fig. S5 displays first cycles (heating and first cooling) of DSC measurements. Thermograms of 1a, 2b and 4a show weak exothermic peaks on cooling which correspond to isotropic to glassy state transitions, whereas molecule 1b decomposes upon melting. Calorimetric data are listed in Table S4.

<table>
<thead>
<tr>
<th>Dye</th>
<th>(T_M^{\circ}C) (^a)</th>
<th>(T_p^{\circ}C) (^b)</th>
<th>(\Delta H) [kJ mol(^{-1})] (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>277</td>
<td>278.64</td>
<td>58.1</td>
</tr>
<tr>
<td>1b</td>
<td>307 (^d)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2a</td>
<td>270</td>
<td>272.04</td>
<td>11.4</td>
</tr>
<tr>
<td>2b</td>
<td>305</td>
<td>306.22</td>
<td>46.9</td>
</tr>
<tr>
<td>3a</td>
<td>168</td>
<td>174.00</td>
<td>16.6</td>
</tr>
<tr>
<td>3b</td>
<td>209</td>
<td>213.82</td>
<td>44.0</td>
</tr>
<tr>
<td>4a</td>
<td>173</td>
<td>176.69</td>
<td>23.8</td>
</tr>
</tbody>
</table>

\(^a\) Melting point determined from the peak onset temperature. \(^b\) Peak temperature. \(^c\) Enthalpy change. \(^d\) Decomposition upon melting.
To calculate thermodynamic data for 2a curve-fitting of the melting peak had to be performed.

**Fig. S6** The first and second phase transitions of 2a fitted with two gaussians.

### 7. Organic thin film transistors and AFM measurements

#### 1.1. Substrates for organic thin film transistor fabrication

Silicon wafers were used as gate electrodes, consisting of boron doped n-type silicon and a 100 nm layer of SiO₂ (gate dielectric; \( C_i = 34 \text{ nF cm}^{-2} \)). These wafers were modified with a thin layer of AlOₓ (8 nm) and a monolayer of \( n \)-tetradecylphosphonic acid (TPA; 1.7 nm; \( C_i = 32.4 \text{ nF cm}^{-2} \)). The wafers were cleaned by spin coating with toluene, acetone and isopropanol (3000 rpm s⁻¹, 30 s), before device preparation.

#### 1.2 Sublimation of organic material and preparation of top contacts

Thin layers of the molecules (30 nm) were sublimed using the AUTO306/FL400 (Boc Edwards) or the EVAP300 (Creaphys). Sublimation took place at about \( 2 \cdot 10^{-6} \text{ mbar} \). The sublimation rate was in the range of 0.2-0.6 nm min⁻¹. Sublimation and substrate temperature were different for each molecule and for compounds 2a and 2b are given in Table S5.

**Table S5** Sublimation temperature, \(^a\) substrate temperature, \(^b\) and the instrument used for processing. \(^c\)

<table>
<thead>
<tr>
<th>Dye</th>
<th>( T_{\text{SUB}} ) [°C] (^a)</th>
<th>( T_{\text{substrate}} ) [°C] (^b)</th>
<th>Instrument (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>160</td>
<td>130</td>
<td>EVAP300</td>
</tr>
<tr>
<td>2b</td>
<td>195</td>
<td>150</td>
<td>EVAP300</td>
</tr>
</tbody>
</table>
Top electrodes were prepared using the same instruments by subliming a 30 nm layer of gold on top of the organic thin film. Shadow masks with square recesses (200 \( \mu \)m x 200 \( \mu \)m) were used providing devices with a length \( L \) and width \( W \) of 100 \( \mu \)m and 200 \( \mu \)m, respectively. The deposition rate was in the range of 0.2-0.6 \( \text{Å s}^{-1} \).

1.3 Atomic force microscopy
Atomic force microscopy (AFM) images were measured with a Multimode 8 AFM (Bruker), operating in tapping mode in air. Cantilevers OMCL-AC160-TS (Olympus) were used (resonance frequency ~ 300 kHz; spring constant ~ 40 Nm\(^{-1}\)).

8. References

9. NMR spectra

Fig. S7 $^1$H NMR of compound 1a (400 MHz, CDCl$_2$CDCl$_2$, 125 °C).

Fig. S8 $^{13}$C NMR of compound 1a (101 MHz, CDCl$_2$CDCl$_2$, 125 °C).
Fig. S9 $^1$H NMR of compound 1b (400 MHz, CDCl$_2$CDCl$_2$, 125 °C).

Fig. S10 $^{13}$C NMR of compound 1b (101 MHz, CDCl$_2$CDCl$_2$, 125 °C).
Fig. S11 $^1$H NMR of compound 2a (400 MHz, CD$_2$Cl$_2$, 25 °C).

Fig. S12 $^{13}$C NMR of compound 2a (101 MHz, CD$_2$Cl$_2$, 25 °C).
Fig. S13 $^1$H NMR of compound 2a$^{m}$ (400 MHz, CD$_2$Cl$_2$, 25 °C).

Fig. S14 $^{13}$C NMR of compound 2a$^{m}$ (101 MHz, CD$_2$Cl$_2$, 25 °C).
Fig. S15 $^1$H NMR of compound 2b (400 MHz, CD$_2$Cl$_2$, 25 °C).

Fig. S16 $^{13}$C NMR of compound 2b (101 MHz, CD$_2$Cl$_2$, 25 °C).
**Fig. S17** $^1$H NMR of compound 3a (400 MHz, CD$_2$Cl$_2$, 25 °C).

**Fig. S18** $^{13}$C NMR of compound 3a (101 MHz, CD$_2$Cl$_2$, 25 °C).
Fig. S19 $^1$H NMR of compound 3a$^m$ (400 MHz, CD$_2$Cl$_2$, 25 °C).

Fig. S20 $^{13}$C NMR of compound 3a$^m$ (101 MHz, CD$_2$Cl$_2$, 25 °C).
Fig. S21 $^1$H NMR of compound 3b (400 MHz, CD$_2$Cl$_2$, 25 °C).

Fig. S22 $^{13}$C NMR of compound 3b (101 MHz, CD$_2$Cl$_2$, 25 °C).
Fig. S23 $^1$H NMR of compound 3b$^m$ (400 MHz, CD$_2$Cl$_2$, 25 °C).

Fig. S24 $^{13}$C NMR of compound 3b$^m$ (101 MHz, CD$_2$Cl$_2$, 25 °C).
Fig. S25 $^1$H NMR of compound 4a (400 MHz, CD$_2$Cl$_2$, 25 °C).

Fig. S26 $^{13}$C NMR of compound 4a (101 MHz, CD$_2$Cl$_2$, 25 °C).
Fig. S27 $^1$H NMR of compound 4a$^m$ (400 MHz, CD$_2$Cl$_2$, 25 °C).

Fig. S28 $^{13}$C NMR of compound 4a$^m$ (101 MHz, CD$_2$Cl$_2$, 25 °C).
10. MS spectra

Fig. S29 ESI MS spectrum of compound 4b.

Fig. S30 ESI MS spectrum of compound 4b′.