Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics. This journal is © the Owner Societies 2019

1

Supporting Information

Dynamic exciton localisation in a pyrene-BODIPY-pyrene dye conjugate

Nina Auerhammer,^a Alexander Schulz,^a Alexander Schmiedel,^a Marco Holzapfel,^a Joscha Hoche^b, Merle I. S. Röhr^a, Roland Mitric,^{b*} Christoph Lambert^{a*}

^aInstitute of Organic Chemistry, Center for Nanosystems Chemistry, Universität Würzburg Am Hubland, D-97074 Würzburg, Germany ^bInstitute of Physical and Theoretical Chemistry, Universität Würzburg Am Hubland, D-97074 Würzburg, Germany

e-mail: christoph.lambert@uni-wuerzburg.de

Synthesis of Py2B



Scheme S1 Synthesis of Py₂B

The synthesis of **Py-7** is based on the work of Marder *et al.*,¹ which used iridiumcatalysed borylation to substitute pyrene in the 2- and 7 position. The alkylation of pyrene by Cul catalysis followed a procedure described by Yang *et al.*² The alkynylation and subsequently deprotection are standard procedures. CA [-]

Synthesis according to literature³

Cul (96.0 mg, 507 μ mol), lithium-*tert*-butoxide (812 mg, 10.1 mmol) and bis(pinacolato)diboron (1.96 mg, 7.71 mmol) were placed in a Schlenk flask. After the flask was evacuated and flushed with nitrogen three times, the mixture was dissolved in dry THF (6 ml) and 1-iodo-3,7-dimethyloctane (1.36 g, 5.07 mmol) was added slowly via syringe. The reaction mixture was stirred for 18 h at room temperature. The suspension was diluted with EA and filtrated through silica. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (eluent: CH_2Cl_2).

Yield: 1.17 g 4.36 mmol 86 % of a colourless liquid.

C₁₆H₃₃BO₂ [268.24]

<u>¹H-NMR</u> (400.0 MHz, CDCl₃):

$$\begin{split} & \delta \text{ [ppm]} = 1.56 - 1.46 \text{ (m, 1 H, C}\underline{\text{H}}\text{)}, \ 1.45 - 1.36 \text{ (m, 1 H, C}\underline{\text{H}}\text{)}, \ 1.35 - 0.97 \text{ (-, 20 H, 4} \\ & \times \text{C}\underline{\text{H}}_2\text{, 4} \times \text{CC}\underline{\text{H}}_3\text{)}, \ 0.86 - 0.82 \text{ (-, 9 H, 3} \times \text{CHC}\underline{\text{H}}_3\text{)}, \ 0.79 - 0.66 \text{ (m, 2 H, C}\underline{\text{H}}_2\text{)}. \end{split}$$

¹³C-NMR (100.6 MHz, CDCl₃):

$$\begin{split} & \delta \text{ [ppm] = 82.8 (Cq,), 39.3 (CH_2), 36.8 (CH_2), 34.9 (CH), 31.0 (CH_2), 28.0 (CH), 24.82 \\ & (CH_2 \text{ and } CH_3), 24.80 (CH_2 \text{ and } CH_3), 22.7 (CH_3), 22.6 (CH_3), 19.2 (CH_3). \end{split}$$

The CH₂- and CH₃-groups are partially overlapping in the 13 C-NMR spectra. Identification was done by using DEPT-135, HMBC and HMQC.

4,4,5,5-Tetramethyl-2-(1-pyrenyl)-1,3,2-dioxaborolane (Py-1)

CA [349666-24-6]

Synthesis according to literature⁴

Under a nitrogen atmosphere pyrene (500 mg, 2.47 mmol) that was filtered through silica beforehand, [{Ir(μ -OMe)(cod)}₂] (17.0 mg, 25.0 μ mol) and 4,4'-di-*tert*-butyl-2,2'-dipyridine (13.0 mg, 48.4 μ mol) were suspended in a Schlenk flask in degased hexane (20 ml). A solution of *bis*(pinacolato)diboron (596 mg, 2.35 mmol) in degassed hexane (30 ml) was dropped to the suspension during 6 h at 80 °C. The reaction mixture was stirred for 18 h at 80 °C and then filtered through silica with CH₂Cl₂ as eluent. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (eluent: CH₂Cl₂ : PE = 1:1).

Yield:471 mg1.44 mmol58 %of a colourless solid. $C_{22}H_{21}BO_2$ [328.21]

<u>¹H-NMR</u> (400.0 MHz, CDCl₃):

δ [ppm] = 8.67 (s, 2 H, 2 × C<u>H</u>), 8.17 (d, ${}^{3}J_{HH}$ = 7.5 Hz, 2 H, 2 × C<u>H</u>), 8.12 (d, ${}^{3}J_{HH}$ = 9.0 Hz, 2 H, 2 × C<u>H</u>), 8.06 (d, ${}^{3}J_{HH}$ = 9.0 Hz, 2 H, 2 × C<u>H</u>), 8.01 (t, ${}^{3}J_{HH}$ = 7.6 Hz, 1 H, C<u>H</u>), 1.52 (s, 12 H, 3 × CC<u>H</u>₃).

Synthesis of 2-Bromopyrene (Py-2)

CA [1714-27-8]

Synthesis according to literature⁴

Py-1 (5.02 g, 15.3 mmol) was dissolved in methanol (166 ml) and copper(II)bromide (10.3 g, 45.9 mmol) in water (166 ml) was added. The mixture was stirred for 72 h at 95 °C. The solution was extracted with diethylether (3×20 ml) and the combined organic phases were washed with brine (3×30 ml). After drying over Na₂SO₄ the solvent was removed under reduced pressure. The oily residue was purified by flash column chromatography (PE).

<u>Yield:</u> 4.02 g 14.3 mmol 93 % of a colourless solid $C_{16}H_9Br$ [281.15]

<u>¹H-NMR</u> (400.0 MHz, CDCl₃):

δ [ppm] = 8.24 (s, 2 H, 2 × C<u>H</u>), 8.17 (d,³ J_{HH} = 7.7 Hz, 2 H, 2 × C<u>H</u>), 8.06 – 7.99 (-, 3 H, 3 × C<u>H</u>), 7.92 (d, ³ J_{HH} = 8.8 Hz, 2 H, 2 × C<u>H</u>).

Synthesis of 2-(3,7-Dimethyloctyl)pyrene (Py-3)

CA [-]

Synthesis according to literature²

 $Pd_2(dba)_3$ (39.0 mg, 42.6 µmol), 2-dicyclohexylphosphino-2',6'-di*iso*propoxybiphenyl (42.6 mg, 91.0 µmol) and sodium-*tert*-butanoxide (620 mg, 6.46 mmol) were placed in a Schlenk flask under a nitrogen atmosphere. 2-(3,7-Dimethyloctyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (523 mg, 1.95 mmol), a solution of **Py-2** (343 mg, 1.22 mmol) in toluene (3.50 ml) and water (0.350 ml) were added via syringe. The

reaction mixture was stirred at 80 °C for 24 h. Afterwards the solution was filtered through silica and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography (eluent: PE).

<u>Yield:</u> 379 mg 1.11 mmol 91 % of a colourless solid $C_{26}H_{30}$ [342.52]

<u>¹H-NMR</u> (400.0 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} &= 8.24 \text{ (d, } {}^{3}J_{\text{HH}} = 7.4 \text{ Hz}, 2 \text{ H}, 2 \times \text{C}\underline{\text{H}}\text{)}, 8.15 - 8.09 \text{ (-, } 6 \text{ H}, 6 \times \text{C}\underline{\text{H}}\text{)}, 8.08 - \\ &= 8.04 \text{ (m, } 1 \text{ H}, \text{C}\underline{\text{H}}\text{)}, 3.24 - 3.07 \text{ (m, } 2 \text{ H}, \text{C}\underline{\text{H}}_{2}\text{)}, 2.05 - 1.65 \text{ (-, } 4 \text{ H}, \text{C}\underline{\text{H}}_{2}, 2 \\ &\times \text{C}\underline{\text{H}}\text{)}, 1.60 - 1.30 \text{ (-, } 6 \text{ H}, 3 \times \text{C}\underline{\text{H}}_{2}\text{)} 1.18 \text{ (d, } {}^{3}J_{\text{HH}} = 6.7 \text{ Hz}, 3 \text{ H}, \text{CHC}\underline{\text{H}}_{3}\text{)}, \\ &= 1.07 \text{ (-, } 6 \text{ H}, \text{CH}(\text{C}\underline{\text{H}}_{3})_{2}\text{)}. \end{split}$$

<u>¹³C-NMR</u> (100.6 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} &= 141.2 \ (\text{C}_{\text{q}}), \ 131.4 \ (\text{C}_{\text{q}}), \ 131.0 \ (\text{C}_{\text{q}}), \ 127.4 \ (\text{CH}), \ 127.3 \ (\text{CH}), \ 125.5 \ (\text{CH}), \\ 125.2 \ (\text{CH}), \ 124.92 \ (\text{CH}), \ 124.86 \ (\text{C}_{\text{q}}), \ 123.3 \ (\text{C}_{\text{q}}), \ 39.8 \ (\text{CH}_2), \ 39.5 \ (\text{CH}_2), \\ 37.4 \ (\text{CH}_2), \ 34.2 \ (\text{CH}_2), \ 32.8 \ (\text{CH}), \ 28.1 \ (\text{CH}), \ 24.9 \ (\text{CH}_2), \ 22.9 \ (\text{CH}_3), \ 22.8 \\ (\text{CH}_3), \ 19.9 \ (\text{CH}_3). \end{split}$$

2-(7-(3,7-Dimethyloctyl)pyrene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**Py-4**) CA [-]

Synthesis according to literature¹

In a schlenk flask [{Ir(μ -OMe)(cod)}₂] (37.3 mg, 56.0 μ mol), 4,4'-di-*tert*-butyl-2,2'dipyridine (29.8 mg, 111 μ mol), *bis*(pinacolato)diboron (952 mg, 3.75 mmol) and **Py-3** (951 mg, 2.78 mmol) were dissolved in dry dioxane (8 ml) under a nitrogen atmosphere. The reaction mixture was stirred for 21 h at 100 °C. Afterwards the catalyst was removed via filtration through silica with CH₂Cl₂ as eluent. The solvent was removed under reduced pressure and the residue was purified by flash chrtomatography (eluent: PE: CH₂Cl₂ = 5:1 \rightarrow 4:1 \rightarrow 3:1).

Yield: 482 mg 1.03 mmol 37 % of a yellow oil

C₃₂H₄₁BO₂ [468.48]

<u>¹H-NMR</u> (400.0 MHz, CDCl₃):

$$\begin{split} &\delta \text{ [ppm]} = 8.61 \text{ (s, 2 H, 2 } \times \text{C}\underline{\text{H}}\text{)}, 8.08 \text{ (d, } {}^{3}J_{\text{HH}} = 8.6 \text{ Hz}, 2 \text{ H}, 2 } \times \text{C}\underline{\text{H}}\text{)}, 8.01 - 7.99 \text{ (-,} \\ &4 \text{ H}, 4 } \times \text{C}\underline{\text{H}}\text{)}, 3.13 - 3.00 \text{ (m, 2 H, C}\underline{\text{H}}\text{_2}\text{)}, 1.91 - 1.50 \text{ (-, 4 H, 2 } \times \text{C}\underline{\text{H}}\text{, C}\underline{\text{H}}\text{_2}\text{)}, \\ &1.47 \text{ (s, 12 H, 4 } \times \text{C}\underline{\text{C}}\underline{\text{H}}\text{_3}\text{)}, 1.43 - 1.14 \text{ (-, 6 H, 3 } \times \text{C}\underline{\text{H}}\text{_2}\text{)}, 1.02 \text{ (d,} \\ &{}^{3}J_{\text{HH}} = 6.6 \text{ Hz}, 3 \text{ H}, \text{C}\text{H}\text{C}\underline{\text{H}}\text{_3}\text{)}, 0.88 \text{ (d, } {}^{3}J_{\text{HH}} = 6.6 \text{ Hz}, 6 \text{ H}, \text{C}\text{H}(\text{C}\underline{\text{H}}\text{_3}\text{)}\text{2}\text{)}. \end{split}$$

13C-NMR (100.6 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} &= 141.9 \ (\text{C}_{\text{q}}), \ 131.9 \ (\text{C}_{\text{q}}), \ 131.3 \ (\text{CH}), \ 130.3 \ (\text{C}_{\text{q}}), \ 127.9 \ (\text{CH}), \ 127.2 \ (\text{CH}), \\ &126.6 \ (\text{C}_{\text{q}}), \ 125.1 \ (\text{CH}), \ 123.2 \ (\text{C}_{\text{q}}), \ 84.3 \ (\text{C}_{\text{q}}), \ 39.8 \ (\text{CH}_2), \ 39.5 \ (\text{CH}_2), \ 37.4 \\ &(\text{CH}_2), \ 34.3 \ (\text{CH}_2), \ 32.8 \ (\text{CH}), \ 28.1 \ (\text{CH}), \ 25.2 \ (\text{CH}_3), \ 24.9 \ (\text{CH}_2), \ 22.9 \\ &(\text{CH}_3), \ 22.8 \ (\text{CH}_3), \ 19.9 \ (\text{CH}_3). \end{split}$$

2-Bromo-7(3,7-dimethyloctyl)pyrene (Py-5)

CA [-]

Br

Synthesis according to literature¹

To a solution of **Py-4** (307 mg, 656 µmol) in methanol (10 ml) and THF (3.5 ml), copper(II)bromide (586 mg, 2.62 mmol) in water (10 ml) was added. The reaction mixture was heated to 110 °C and stirred for 5 d. Water was added to the mixture and the solution was extracted with Et₂O. The combined organic layers were washed with brine (2 × 40 ml) and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (eluent: PE).

<u>Yield:</u> 209 mg 496 μ mol 76 % of a colourless solid C₂₆H₂₉Br [421.41]

<u>¹H-NMR</u> (400.0 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} &= 8.25 \text{ (s, 2 H, 2 × C<u>H), 8.05 - 8.02 (-, 4 H, 4 × C<u>H), 7.94 (d, {}^{3}J_{\text{HH}} = 9.0 \text{ Hz}, \\ &2 \text{ H, 2 × C<u>H}, 3.13 - 3.00 \text{ (m, 2 H, CH_2), 1.91 - 1.62 (m, 2 H, CH_2), 1.59 - 1.49 (-, 2 H, 2 × C<u>H), 1.45 - 1.13 (-, 6 H, 3 × CH_2), 1.02 (d, {}^{3}J_{\text{HH}} = 6.6 \text{ Hz}, \\ &3 \text{ H, CHC}\underline{\text{H}_3}\text{), 0.87 (d, {}^{3}J_{\text{HH}} = 6.6 \text{ Hz}, 6 \text{ H, CH}(C\underline{\text{H}_3}\text{)_2}\text{).} \end{split}$$
</u></u></u></u>

<u>¹³C-NMR</u> (100.6 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} &= 141.7 \ (\text{C}_{\text{q}}), \ 132.6 \ (\text{C}_{\text{q}}), \ 131.1 \ (\text{C}_{\text{q}}), \ 128.6 \ (\text{CH}), \ 127.1 \ (\text{CH}), \ 126.4 \ (\text{CH}), \\ 126.0 \ (\text{CH}), \ 123.4 \ (\text{C}_{\text{q}}), \ 122.9 \ (\text{C}_{\text{q}}), \ 119.56 \ (\text{C}_{\text{q}}), \ 39.8 \ (\text{CH}_2), \ 39.5 \ (\text{CH}_2), \\ 37.4 \ (\text{CH}_2), \ 34.2 \ (\text{CH}_2), \ 32.8 \ (\text{CH}), \ 28.1 \ (\text{CH}), \ 24.9 \ (\text{CH}_2), \ 22.9 \ (\text{CH}_3) \ 22.8 \\ (\text{CH}_3), \ 19.9 \ (\text{CH}_3). \end{split}$$

2-(Trimethylsilyl-ethynyl)-7-(3,7-dimethyloctyl)pyrene (**Py**)

CA [-]

Synthesis according to literature^{5, 6}

Bis(benzonitrile)palladium(II)chloride (846 µg, 2.21 µmol), Cul (140 µg, 0.740 µmol) and **Py-5** (31.0 mg, 74.0 µmol) were dissolved in dioxane (1 ml) under a nitrogen atmosphere. Di*iso*propylamine (0.630 µl, 4.41 µmol), tri-*tert*butylphosphine (1 M in toluene, 4.41 µl, 4.41 µmol) and trimethylsilylacetylene (0.0150 µl, 103 µmol) were added via syringe. After stirring for 24 h at 80 °C, the solution was cooled to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and washed with water. The aqueous phase was extracted with CH₂Cl₂ (2 × 30 ml) and the combined organic layers were dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (eluent: PE).

<u>Yield</u>: 29.9 mg 68.2 μ mol 93 % of a yellow solid C₃₁H₃₈Si [438.72]

MALDI-TOF MS (POS, DCTB : $CHCl_3 = 1 : 3$):

calc. for $C_{31}H_{38}Si: m/z = 438.274$ found: m/z = 438.244

<u>¹H-NMR</u> (400.0 MHz, CDCl₃):

δ [ppm] = 8.24 (s, 2 H, 2 × C<u>H</u>), 8.03 – 8.00 (-, 4 H, 4 × C<u>H</u>), 7.97 (d, ³J_{HH} = 8.8 Hz, 2 H, 2 × C<u>H</u>), 3.13 – 2.96 (m, 2 H, C<u>H</u>₂), 1.90 – 1.61 (m, 2 H, C<u>H</u>₂), 1.59 – 1.13 (-, 8 H, 2 × C<u>H</u>, 3 × C<u>H</u>₂), 1.01 (d, ³J_{HH} = 6.5 Hz, 3 H, CHC<u>H</u>₃), 0.87 (d, ³J_{HH} = 6.6 Hz, 6 H, CH(C<u>H</u>₃)₂), 0.38 (s, 9 H, Si(C<u>H</u>₃)₃).

<u>¹³C-NMR</u> (100.6 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} &= 141.9 \ (\text{C}_{\text{q}}), \ 131.5 \ (\text{C}_{\text{q}}), \ 130.8 \ (\text{C}_{\text{q}}), \ 128.1 \ (\text{CH}), \ 128.0 \ (\text{CH}), \ 127.0 \ (\text{CH}), \\ 125.6 \ (\text{CH}), \ 124.5 \ (\text{C}_{\text{q}}), \ 123.0 \ (\text{C}_{\text{q}}), \ 120.1 \ (\text{C}_{\text{q}}), \ 106.0 \ (\text{C}_{\text{q}}), \ 94.5 \ (\text{C}_{\text{q}}), \ 39.8 \\ (\text{CH}_2), \ 39.5 \ (\text{CH}_2), \ 37.3 \ (\text{CH}_2), \ 34.2 \ (\text{CH}_2), \ 32.8 \ (\text{CH}), \ 28.1 \ (\text{CH}), \ 24.9 \\ (\text{CH}_2), \ 22.9 \ (\text{CH}_3), \ 22.8 \ (\text{CH}_3), \ 19.9 \ (\text{CH}_3), \ 0.22 \ (\text{CH}_3). \end{split}$$

2-Ethynyl-7-(3,7-dimethyloctyl)pyrene (Py-7)

CA [-]

Synthesis according to literature ⁵

Under a nitrogen atmosphere **Py** (50.0 mg, 114 μ mol) was solved in dry THF and a solution of TBAF (1 M in THF, 0.260 ml, 0.260 mmol) was added. After a reaction time of 2 h at room temperature the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and washed with water (3 × 10 ml). The organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure.

<u>Yield</u>: 39.2 mg 107 μ mol 94 % of a brown oil C₂₈H₃₀ [366.54] MALDI-TOF MS (POS, DCTB : CHCl₃ = 1 : 3): calc. for C₂₈H₃₀: m/z = 366.235 found: m/z = 366.235 <u>1H-NMR</u> (400.0 MHz, CDCl₃):

δ [ppm] = 8.26 (s, 2 H, 2 × C<u>H</u>), 8.04 – 8.00 (-, 4 H, 4 × C<u>H</u>), 8.01 (d, ³J_{HH} = 9.0 Hz, 2 H, 2 × C<u>H</u>), 3.23 (s, 1 H, ≡ C<u>H</u>), 3.13 – 2.97 (m, 2 H, C<u>H</u>₂) 1.91 – 1.61 (m, 2 H, C<u>H</u>₂), 1.60 – 1.49 (-, 2 H, 2 × C<u>H</u>), 1.45 – 1.13 (-, 6 H, 3 × C<u>H</u>₂), 1.02 (d, ³J_{HH} = 6.6 Hz, 3 H, CHC<u>H</u>₃), 0.87 (d, ³J_{HH} = 6.6 Hz, 6 H, CH(C<u>H</u>₃)₂).

13C-NMR (100.6 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} &= 142.0 \ (\text{C}_{\text{q}}), \ 131.5 \ (\text{C}_{\text{q}}), \ 130.9 \ (\text{C}_{\text{q}}), \ 128.2 \ (\text{CH}), \ 128.1 \ (\text{CH}), \ 126.9 \ (\text{CH}), \\ 125.7 \ (\text{CH}), \ 124.7 \ (\text{C}_{\text{q}}), \ 122.9 \ (\text{C}_{\text{q}}), \ 119.0 \ (\text{C}_{\text{q}}), \ 84.5 \ (\text{C}_{\text{q}}), \ 77.4 \ (\text{CH}), \ 39.8 \\ (\text{CH}_2), \ 39.5 \ (\text{CH}_2), \ 37.4 \ (\text{CH}_2), \ 34.2 \ (\text{CH}_2), \ 32.8 \ (\text{CH}), \ 28.1 \ (\text{CH}), \ 24.9 \\ (\text{CH}_2), \ 22.9 \ (\text{CH}_3), \ 22.8 \ (\text{CH}_3), \ 19.9 \ (\text{CH}_3). \end{split}$$

Trimer Py2B



Synthesis according to literature⁷

In a nitrogen atmosphere 1,1-bis(diphenylphosphino)ferrocene dichloropalladium(II) complex with dichloromethane (1.59 mg, 1.95 μ mol), Cul (0.742 mg, 3.90 μ mol) and **Bodipy-1**⁸ (22.8 mg, 32.4 μ mol) were dissolved in a degased mixture of THF/triethylamine (5:2). The mixture was again degassed and pyrene **Py-7** (25.0 mg, 68.2 μ mol) was added. After stirring for four days at rt the solution was heated to 50 °C and stirred for additional 24 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (eluent: PE

 \rightarrow PE:CH₂Cl₂ 7:3 \rightarrow PE:CH₂Cl₂ 1:1 \rightarrow CH₂Cl₂ \rightarrow EA). For further purification the resulting product was precipitated from CH₂Cl₂/acetonitrile.

Yield:19.2 mg16.3 μ mol50 %of a dark-blue solid. $C_{83}H_{91}BF_2N_2O$ [1181.43]HRMS (ESI):[M*+] = $C_{83}H_{91}BF_2N_2O^{*+}$; calc.:1180.719996; found:1180.71776(Δ = 1.89 ppm)

<u>¹H-NMR</u> (400.0 MHz, CD₂Cl₂):

$$\begin{split} & \delta \text{ [ppm]} = 8.00 - 7.98 \ (-, \ 8 \ H; \ 8 \ \times C\underline{H}), \ 7.96 - 7.93 \ (d, \ ^3J_{\text{HH}} = 9.0 \ \text{Hz}, \ 4 \ \text{H}, \ 4 \ \times C\underline{H}), \\ & 7.83 \ (s, \ 4 \ \text{H}, \ 4 \ \times C\underline{H}), \ 7.16 \ (m, \ 2 \ \text{H}, \ 2 \ \times C\underline{H}), \ 7.07 \ (m, \ 2 \ \text{H}, \ 2 \ \times C\underline{H}), \ 3.97 \ (d, \ ^3J_{\text{HH}} = 5.7 \ \text{Hz}, \ 2 \ \text{H}, \ OC\underline{H_2}), \ 2.76 \ (s, \ 6 \ \text{H}, \ 2 \ \times CC\underline{H_3}), \ 2.86 \ (m, \ 4 \ \text{H}, \ 2 \ \times C\underline{H_2}), \\ & 1.84 - 0.97 \ (-, \ 47 \ \text{H}, \ 5 \ \times C\underline{H}, \ 12 \ \times C\underline{H_2}, \ 2 \ \times CC\underline{H_3}, \ 2 \ \times CHC\underline{H_3}, \ 2 \ \times CH\underline{CH_3}, \ 2 \ \times CH\underline{CH_3}), \\ & 0.87 \ (m, \ 12 \ \text{H}, \ 2 \ \times C(C\underline{H_3})_2). \end{split}$$

13C-NMR (150.6 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} &= 161.3 \ (\text{C}_{\text{q}}), \ 158.1 \ (\text{C}_{\text{q}}), \ 143.9 \ (\text{C}_{\text{q}}), \ 142.6 \ (\text{C}_{\text{q}}), \ 141.6 \ (\text{C}_{\text{q}}), \ 131.8 \ (\text{C}_{\text{q}}), \ 131.3 \\ & (\text{C}_{\text{q}}), \ 130.8 \ (\text{C}_{\text{q}}), \ 129.2 \ (\text{CH}), \ 127.9 \ (\text{CH}), \ 127.2 \ (\text{CH}), \ 126.8 \ (\text{CH}), \ 126.3 \\ & (\text{C}_{\text{q}}), \ 125.5 \ (\text{CH}), \ 124.1 \ (\text{C}_{\text{q}}), \ 122.9 \ (\text{C}_{\text{q}}), \ 120.3 \ (\text{C}_{\text{q}}), \ 116.1 \ (\text{C}_{\text{q}}), \ 115.3 \ (\text{CH}), \\ & 97.4 \ (\text{C}_{\text{q}}), \ 82.0 \ (\text{C}_{\text{q}}), \ 71.0 \ (\text{CH}_2), \ 39.6 \ (\text{CH}_2), \ 39.5 \ (\text{CH}), \ 39.4 \ (\text{CH}_2), \ 37.2 \\ & (\text{CH}_2), \ 33.9 \ (\text{CH}_2), \ 32.7 \ (\text{CH}), \ 30.7 \ (\text{CH}_2), \ 29.3 \ (\text{CH}_2), \ 28.1 \ (\text{CH}), \ 24.8 \\ & (\text{CH}_2), \ 24.0 \ (\text{CH}_2), \ 23.2 \ (\text{CH}_2), \ 22.8 \ (\text{CH}_3), \ 22.7 \ (\text{CH}_3), \ 19.7 \ (\text{CH}_3), \ 14.3 \\ & (\text{CH}_3), \ 13.9 \ (\text{CH}_3), \ 13.7 \ (\text{CH}_3), \ 11.3 \ (\text{CH}_3). \end{split}$$



Fig. S1 Fluorescence excitation anisotropy spectrum in poly-THF (black triangles) and absorption spectrum of Py_2B in CH_2Cl_2 (red solid line).



Fig. S2 Chirp corrected transient absorption spectra of Py_2B (a) in CH_2CI_2 at 17200 cm⁻¹ excitation. b) Evolution associated difference spectra from global fit of the TA data. c) Decay associated difference spectra from global fit of the TA data. d) – e)

Transient decay profiles (black circles) at selected wavenumbers and global fit (red solid line).

State	Energy/ cm ⁻¹	Osci ll ator Strength	µ _× ∕D	μ y/D	μ _z /D	Transition Density $S_0 \rightarrow State$	State	Energy/ cm ⁻¹	Osci ll ator Strength	µ x∕D	µ,∕D	μ _z /D	Transition Density $S_0 \rightarrow State$
S1	19810	1,84	14,05	0,01	0,01	¥	S ₁₁	32510	3,30	-14,68	0,01	0,01	- Anita Che
S ₂	26351	0,01	0,02	0,24	0,03		S ₁₂	32791	0,08	-0,01	2,26	- 0,15	ep in the second
S ₃	26352	0,01	-0,03	0,24	0,03	-#	S ₁₃	33569	0,07	-0,01	-2,11	0,06	BARAN
S4	26638	0,01	-0,03	0,77	-0,05	- A MAR	S ₁₄	33723	0,01	0,20	-0,01	0,01	+## ** *
S_5	26684	0,13	3,19	0,01	-0,01	-	S ₁₅	34722	0,01	-0,01	-0,07	-0,01	
S_6	27991	0,13	-0,01	- 3,15	-0,02	***	S ₁₆	34722	0,01	-0,01	- 0,07	-0,01	-==
S7	28024	0,01	-0,03	0,01	0,01	spillings	S ₁₇	37638	0,08	-0,01	2,06	-0,12	***
S ₈	30945	0,01	-0,01	0,24	0,70	-+\$\$\$\$\$\$+-	S ₁₈	37837	0,13	2,73	0,01	-0,01	
S ₉	32342	0,01	- 0,34	- 0,07	-0,01		S ₁₉	37869	0,01	- 0,01	0,32	-0,09	
S ₁₀	32343	0,01	0,01	-0,21	-0,02	****	S ₂₀	38208	0,08	-0,01	2,03	0,29	@ \$

Fig. S3 Simulated absorption energy, oscillator strengths, cartesian components of the transition dipole moments and transition densities between the ground state and the corresponding excited state at the level of AM1 CIS.

State	Energy/ cm ⁻¹	Oscillator Strength	⊠ _x /D	⊠ _y /D	⊠₂/D	Transition Density S ₀ I _State	State	Energy/ cm ⁻¹	Oscillator Strength	⊠ _x /D	⊠y/D	⊠₂/D	Transition Density S₀ I _State
S ₁	21373	1.68	12.96	0.03	0.03	¥	S ₁₁	35327	3.66	-14.84	0.03	0.03	- Contraction
S ₂	27987	0.08	0.03	-2.41	-0.05		S ₁₂	36375	0.01	-0.03	0.84	-0.05	Onijas
S ₃	28713	0.27	4.5	0.03	0.03	- ****** ***	S ₁₃	37585	0.01	0.25	-0.03	-0.03	♦ ₩ €
S ₄	30003	0.01	-0.03	0.15	0.03		S ₁₄	37585	0.29	0.03	4.02	0.03	*
S ₅	30003	0.01	0.03	0.08	0.03		S ₁₅	38311	0.02	0.03	-1.17	0.03	+ \$\{\}00\}\$ \$\$\$\$\$\$\$\$\$
S ₆	31052	0.01	0.03	-0.03	0.03	+} \$ \$\$\$\$\$\$\$\$	S ₁₆	39037	0.03	1.3	0.03	0.03	
S7	32342	0.13	2.87	-0.03	0.03	Bijde	S ₁₇	39440	0.01	-0.03	0.03	0.03	♦₩♦
S ₈	32423	0.01	0.03	-0.36	-0.03		S ₁₈	39440	0.03	-0.03	-1.17	-0.03	*
S ₉	33391	0.01	-0.1	0.03	0.03		S ₁₉	40408	0.02	-0.89	-0.03	0.03	+ ;;;;;;;;;;; ;;;;;;;;;;;;;;;;;;;;;;;;;
S ₁₀	33391	0.03	-0.03	-1.47	-0.03		S ₂₀	40408	0.13	-0.03	-2.62	-0.03	*

Fig. S4 Simulated absorption energy, oscillator strengths, cartesian components of the transition dipole moments and transition densities between the ground state and the corresponding excited state at the level of TDDFT (CAM-B3LYP/def2-SVP).

References

- 1 A. G. Crawford, Z. Liu, I. A. I. Mkhalid, M.-H. Thibault, N. Schwarz, G. Alcaraz, A. Steffen, J. C. Collings, A. S. Batsanov, J. A. K. Howard and T. B. Marder, *Chem.-Eur. J.*, 2012, **18**, 5022-5035.
- 2 C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czyzewska, P. G. Steel, T. B. Marder and L. Liu, *Angew. Chem., Int. Ed.*, 2012, **51**, 528-532.
- 3 N. A. Schopf, Master Thesis, Würzburg, 2014.
- 4 J. Ehbets, Diploma thesis, Universität Würzburg, 2012.
- 5 D. Rausch and C. Lambert, *Org. Lett.*, 2006, **8**, 5037-5040.
- 6 T. Hundertmark, A. F. Littke, S. L. Buchwald and G. C. Fu, *Org. Lett.*, 2000, **2**, 1729-1731.
- 7 Q. Huaulme, A. Mirloup, P. Retailleau and R. Ziessel, *Org. Lett.*, 2015, **17**, 2246-2249.
- 8 B. C. Popere, A. M. Della Pelle and S. Thayumanavan, *Macromolecules*, 2011, **44**, 4767-4776.