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Excited States and Spin-Orbit Coupling in Chalcogen Substituted Perylene Diimides and their Radical Anions.

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1 Materials and Methods

NMR Spectroscopy

 Avance III HD 400 FT-Spectrometer (¹H: 400.13 MHz, ¹³C: 100.61 MHz) with a Bruker Ultrashield magnet

- Avance III HD 400 FT-Spectrometer (¹H: 400.03 MHz, ¹³C: 100.59 MHz) with a Bruker Ascend magnet
- Avance III HD 600 FT-Spectrometer (¹H: 600.13 MHz, ¹³C: 150.90 MHz) with an Oxford Instruments magnet
- Avance III HD 600 FT-Spectrometer (¹H: 600.43 MHz, ¹³C: 150.98 MHz) with a Bruker Ascend magnet

¹H and ¹³C spectra were acquired using one of the spectrometer listed above with sample concentrations of > 0.1 mM in deuterated solvents (, CD_2CI_2 and $CDCI_3$). All solvents were used as received. Chemical shifts for the proton spectra are given in ppm relative to the residual nondeuterated solvent signal (CH_2CI_2 : δ 5.32 CHCI₃: δ 7.26) and for the carbon spectra relative to the ¹³C isotop signal of the solvent (¹³C: CH_2CI_2 : δ 53.84, $CHCI_3$: δ 77.16).¹ The abbreviations used for assigning the spin multiplicities and C-atoms are: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, prim = primary, sec = secondary, tert = tertiary, quart = quarternary. Overlapping signals of chemically non-equivalent protons in proton NMR spectra that could not be assigned to first-order couplings are given as m'. The coupling constants are given in Hertz (Hz). Order of description for ¹H NMR spectra: chemical shift (spin multiplicity, coupling constant, number of protons, assignment).

Mass Spectrometry

- Bruker Daltonics microTOF focus (ESI)
- Bruker Daltonics autoflex II LRF (MALDI)
- Bruker Daltonics UltrafleXtreme (MALDI)

Mass spectra were recorded with a Bruker Daltonics autoflex II LRF or a Bruker Daltonics UltrafleXtreme (MALDI) in positive mode (POS) using a DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) matrix. High resolution mass spectra were recorded with a Bruker Daltonic microTOF focus (ESI). All mass spectra peaks are reported as m/z. For calculation of the respective mass values of the isotopic distributions the software Compass 1.1 from Bruker Daltonics GmbH (Bremen, Germany) was used. Calculated (calc.) and measured (found) peak values refer to the most intense peak of the isotopic distributions or the monoisotopic mass unless stated otherwise.

Solvent Purification System (SPS)

Inert anhydrous solvent dispensing system

- Model: PS-MD-6/7-EN

- Drying Columns: dual purifying columns design / polystyrene / medium density / 101 × 635 mm / 4 L internal volume
- 29/30 stainless steel glassware adaptors
- Particle filter (7 micron)
- 17 L solvent reservoirs for (DCM, DMF, Et₂O, toluene, THF)

HPLC grade and stabilizer free solvents were used to fill the reservoirs. The dry solvents were filled into flame-dried Schlenk flasks and degassed prior use by bubbling dry nitrogen gas through it or by three freeze-pump-thaw cycles.

2 Synthesis

All reactions were performed in standard glass ware. All chemicals were purchased from commercial suppliers and were used without further purification. For reactions performed under nitrogen atmosphere flame-dried Schlenk flasks were used. Nitrogen was dried over Sicapent® from Merck and oxygen was removed via copper catalyst R3-11 from BASF. Dry solvents were freshly taken from the SPS, non-dry solvents were destilled and stored in the dark. Column chromatography and thin layer chromatography were performed on silica gel ($40 - 63 \mu m$, Macherey-Nagel) in wet-packed glass columns and TLC plates (Macherey-Nagel), respectively. Preparative thin layer chromatography was performed on prepacked silica gel plates ($20 \times 20 cm$, 500 microns) from ANALTECH.

Reagents

Perylene-3,4,9,10-tetracarboxylic tetrabutylester, 1,7-dibromoperylene-3,4,9,10tetracarboxylic tetrabutylester and 1,7-dibromoperylene-3,4,9,10-tetracarboxylic dibutylester monoanhydride were synthesized according to literature.²



Synthetic Route of the Brominated Perylenediimide Building Block

Figure S 1: Synthetic route of the brominated building block PDI(Br)2.

Synthesis of **1**,**7**-dibromo-*N*-(**2**,**5**-di-tert-butylphenyl)-**9**,**10**-di(butyl carboxylate) perylene monoimide (**2**)



Synthesis according to literature.²

Under a nitrogen atmosphere, **1** (54.0 mg, 79.4 μ mol), 2,5-di-*tert*-butylaniline (20.0 mg, 97.4 μ mol), and acetic acid (25.0 μ l, 436 μ mol) were dissolved in NMP (1 mL) and degassed for 15 min. After stirring for 2 d at 120 °C the mixture was poured into water and filtrated. The residue was washed with water and purified via flash column chromatography (eluent: DCM).

Yield: 50.6 mg (58.3 µmol, 73 %) of a red solid.

 $C_{46}H_{45}Br_2NO_6$ [867.66]

¹**H-NMR** (400 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} = & 9.28 \text{ (d, } ^3J_{\text{HH}} = 8.0 \text{ Hz}, \text{ 1H}), \ 9.25 \text{ (d, } ^3J_{\text{HH}} = 7.9 \text{ Hz}, \text{ 1H}), \ 8.93 \text{ (s, 1H}), \ 8.72 \text{ (d,} \\ ^3J_{\text{HH}} = 8.1 \text{ Hz}, \text{ 1H}), \ 8.36 \text{ (s, 1H)}, \ 8.16 \text{ (d, } ^3J_{\text{HH}} = 8.0 \text{ Hz}, \text{ 1H}), \ 7.60 \text{ (d,} \\ ^3J_{\text{HH}} = 8.6 \text{ Hz}, \text{ 1H}), \ 7.47 \text{ (dd, } ^3J_{\text{HH}} = 8.5 \text{ Hz}, \ ^4J_{\text{HH}} = 2.3 \text{ Hz}, \text{ 1H}), \ 6.99 \text{ (d,} \\ ^4J_{\text{HH}} = 2.1 \text{ Hz}, \text{ 1H}), \ 4.39 - 4.31 \text{ (m', 4H)}, \ 1.85 - 1.74 \text{ (m', 4H)}, \ 1.54 - 1.45 \text{ (m', 4H)}, \ 1.32 \text{ (s, 9H)}, \ 1.31 \text{ (s, 9H)}, \ 1.03 - 0.97 \text{ (m', 6H)}. \end{split}$$

¹³**C-NMR** (100 MHz, CDCl₃):

$$\begin{split} \delta \, [\text{ppm}] = & 167.9\,(\text{C}_{\text{q}}), 167.1\,(\text{C}_{\text{q}}), 164.3\,(\text{C}_{\text{q}}), 163.8\,(\text{C}_{\text{q}}), 150.3\,(\text{C}_{\text{q}}), 143.9\,(\text{C}_{\text{q}}), 138.3\,(\text{CH}), \\ & 137.0\,(\text{CH}), \, 134.4\,(\text{C}_{\text{q}}), \, 133.9\,(\text{C}_{\text{q}}), \, 132.6\,(\text{C}_{\text{q}}), \, 132.1\,(\text{C}_{\text{q}}), \, 131.9\,(\text{C}_{\text{q}}), \, 131.7 \\ & (\text{C}_{\text{q}}), \, 131.0\,(\text{C}_{\text{q}}), \, 130.7\,(\text{C}_{\text{q}}), \, 130.5\,(\text{CH}), \, 129.4\,(\text{C}_{\text{q}}), \, 129.2\,(\text{CH})\,\, 129.0\,(\text{CH}), \\ & 128.3\,(\text{CH}), \, 128.3\,(\text{CH}), \, 127.8\,(\text{CH}), \, 127.2\,(\text{C}_{\text{q}}), \, 127.0\,(\text{C}_{\text{q}}), \, 126.6\,(\text{CH}), \, 122.6 \\ & (\text{C}_{\text{q}}), \, 122.4\,(\text{C}_{\text{q}}), \, 120.4\,(\text{C}_{\text{q}}), \, 119.6\,(\text{C}_{\text{q}}), \, 66.2\,(\text{CH}_2), \, 65.9\,(\text{CH}_2), \, 35.7\,(\text{C}_{\text{q}}), \, 34.4 \\ & (\text{C}_{\text{q}}), \, 31.9\,(\text{CH}_3), \, 31.3\,(\text{CH}_3), \, 30.7\,(\text{CH}_2), \, 30.7\,(\text{CH}_2), \, 19.4\,(\text{CH}_2), \, 19.3\,(\text{CH}_2), \\ & 13.9\,(2\times\text{CH}_3). \end{split}$$

MALDI-MS (pos.):

calc.: [M]⁺ 867.16 m/z found: [M]⁺ 867.19 m/z

Synthesis of **1,7-dibromo-***N***-(2,5-di-tert-butylphenyl)-3,4-anhydride perylene monoimide** (3)



Synthesis according to literature.²

Compound **2** (1.00 g, 1.15 mmol) and *p*-toluenesulfonic acid monohydrate (1.10 g, 5.78 mmol) were dissolved in toluene (8 mL) and stirred for 18 h at 90 °C. The solvent was removed *in vacuo* and the residue was purified via flash column chromatography (eluent: DCM).

Yield: 700 mg (949 µmol, 83 %) of a red solid.

 $C_{38}H_{27}Br_2NO_5$ [737.43]

¹**H-NMR** (400 MHz, CDCl₃):

$$\begin{split} & \delta \text{[ppm]} = 9.58 \text{ (d, } {}^{3}J_{\text{HH}} = 8.2 \text{ Hz}, \text{ 1H}\text{)}, 9.56 \text{ (d, } {}^{3}J_{\text{HH}} = 8.1 \text{ Hz}, \text{ 1H}\text{)}, 9.00 \text{ (s, 1H)}, 8.98 \text{ (s, 1H)}, 8.80 \text{ (d, } {}^{3}J_{\text{HH}} = 8.1 \text{ Hz}, \text{ 1H}\text{)}, 8.76 \text{ (d, } {}^{3}J_{\text{HH}} = 8.1 \text{ Hz}, \text{ 1H}\text{)}, 7.62 \text{ (d, } {}^{3}J_{\text{HH}} = 8.6 \text{ Hz}, \text{ 1H}\text{)}, 7.49 \text{ (dd, } {}^{3}J_{\text{HH}} = 8.6 \text{ Hz}, {}^{4}J_{\text{HH}} = 2.3 \text{ Hz}, \text{ 1H}\text{)}, 6.99 \text{ (d, } {}^{4}J_{\text{HH}} = 2.2 \text{ Hz}, \text{ 1H}\text{)}, 1.33 \text{ (s, 9H)}, 1.31 \text{ (s, 9H)} \end{split}$$

¹³C-NMR (100 MHz, CDCl₃):

$$\begin{split} \delta \text{[ppm]} = & 163.9 \ (\text{C}_{\text{q}}), \ 163.4 \ (\text{C}_{\text{q}}), \ 159.3 \ (\text{C}_{\text{q}}), \ 159.0 \ (\text{C}_{\text{q}}), \ 150.5 \ (\text{C}_{\text{q}}), \ 143.9 \ (\text{C}_{\text{q}}), \ 140.0 \\ & (\text{CH}), \ 138.6 \ (\text{CH}), \ 134.9 \ (\text{C}_{\text{q}}), \ 134.7 \ (\text{C}_{\text{q}}), \ 132.8 \ (\text{C}_{\text{q}}), \ 132.7 \ (\text{C}_{\text{q}}), \ 132.3 \ (\text{CH}), \\ & 132.2 \ (\text{C}_{\text{q}}), \ 130.7 \ (\text{CH}), \ 129.9 \ (\text{C}_{\text{q}}), \ 129.7 \ (\text{C}_{\text{q}}), \ 129.3 \ (\text{CH}), \ 129.3 \ (\text{C}_{\text{q}}), \ 129.1 \end{split}$$

(CH), 128.9 (CH), 127.6 (CH), 127.5 (C_q), 126.8 (CH), 124.2 (C_q), 123.7 (C_q), 121.9 (C_q), 120.9 (C_q), 119.1 (C_q), 118.8 (C_q), 35.7 (C_q), 34.4 (C_q), 31.9 (CH₃), 31.3 (CH₃).

MALDI-MS (pos.):

calc.: [M]⁺⁺ 737.02 m/z found: [M]⁺⁺ 737.04 m/z

Synthesis of PDI(Br)2



Synthesis according to literature.²

Under a nitrogen atmosphere, compound **3** (100 mg, 136 μ mol), aniline (27.0 μ l, 298 μ mol) and acetic acid (43.0 μ l, 752 μ mol) were dissolved in NMP (0.5 mL) and degassed for 15 min. After stirring for 4 h at 80 °C, the mixture was poured into water and filtrated. The residue was washed with water and purified via flash column chromatography (eluent: DCM).

Yield: 105 mg (129 μ mol, 95 %) of a red solid.

 $C_{44}H_{32}Br_2N_2O_4$ [812.54]

¹**H-NMR** (400 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} = & 9.56 \text{ (d, } ^{3}J_{\text{HH}} = 8.1 \text{ Hz}, \text{ 2H} \text{)}, 9.00 \text{ (s, 1H)}, 8.97 \text{ (s, 1H)}, 8.78 \text{ (d, } ^{3}J_{\text{HH}} = 8.1 \text{ Hz}, \\ 1\text{H} \text{)}, 8.77 \text{ (d, } ^{3}J_{\text{HH}} = 8.1 \text{ Hz}, 1\text{H} \text{)}, 7.63 - 7.57 \text{ (m', 3H)}, 7.54 \text{ (m, 1H)}, 7.49 \text{ (dd,} \\ ^{3}J_{\text{HH}} = 8.6 \text{ Hz}, \, ^{4}J_{\text{HH}} = 2.2 \text{ Hz}, 1\text{H} \text{)}, 7.37 - 7.33 \text{ (m', 2H)}, 7.02 \text{ (d, } ^{3}J_{\text{HH}} = 2.2 \text{ Hz}, \\ 1\text{H} \text{)}, 1.33 \text{ (s, 9H)}, 1.31 \text{ (s, 9H)}. \end{split}$$

¹³C-NMR (100 MHz, CDCl₃):

$$\begin{split} \delta \text{ [ppm]} = & 164.1 \ (\text{C}_{\text{q}}), \ 163.6 \ (\text{C}_{\text{q}}), \ 163.3 \ (\text{C}_{\text{q}}), \ 162.7 \ (\text{C}_{\text{q}}), \ 150.5 \ (\text{C}_{\text{q}}), \ 143.9 \ (\text{C}_{\text{q}}), \ 138.54 \\ (\text{CH}), \ 138.49 \ (\text{CH}), \ 134.8 \ (\text{C}_{\text{q}}), \ 133.6 \ (\text{C}_{\text{q}}), \ 133.5 \ (\text{C}_{\text{q}}), \ 133.4 \ (\text{C}_{\text{q}}), \ 133.3 \ (\text{C}_{\text{q}}), \\ & 132.3 \ (\text{C}_{\text{q}}), \ 130.7 \ (\text{CH}), \ 130.6 \ (\text{CH}), \ 129.72 \ (\text{CH}), \ 129.71 \ (\text{C}_{\text{q}}), \ 129.66 \ (\text{C}_{\text{q}}), \\ & 129.3 \ (\text{CH}), \ 129.1 \ (\text{CH}), \ 128.91 \ (\text{CH}), \ 128.87 \ (\text{CH}), \ 128.6 \ (\text{CH}), \ 127.7 \ (\text{CH}), \\ & 127.54 \ (\text{C}_{\text{q}}), \ 127.52 \ (\text{C}_{\text{q}}), \ 126.8 \ (\text{CH}), \ 123.7 \ (\text{C}_{\text{q}}), \ 123.4 \ (\text{C}_{\text{q}}), \ 123.3 \ (\text{C}_{\text{q}}), \ 123.0 \\ & (\text{C}_{\text{q}}), \ 121.3 \ (\text{C}_{\text{q}}), \ 121.1 \ (\text{C}_{\text{q}}), \ 35.7 \ (\text{C}_{\text{q}}), \ 31.9 \ (\text{CH}_3), \ 31.4 \ (\text{CH}_3). \end{split}$$

ESI-HR-MS (pos.):

calc.: [M+Na] ^{.+} 835.0606 m/z	
found: [M+Na] ^{.+} 835.0598 m/z	∆ = 0.96 ppm



Synthesis according to literature.²

Under a nitrogen atmosphere, **PDI(Br)**₂ (50.0 mg, 61.5 µmol), 18-crown-6 (146 mg,552 µmol) and potassium carbonate (45.9 mg, 332 µmol) were dissolved in dry, degassed toluene (4.00 mL). The reaction mixture was stirred for 30 minutes at room temperature and then for 4 hours at 95 °C. The mixture was then cooled down to room temperature and the solvent was removed *in vacuo*. The residue was dissolved DCM and washed three times with water. The organic phase was dried over magnesium sulphate and the solvent was removed *in vacuo*. The crude product was purified via column chromatography (DCM) and via preparative thin layer chromatography (DCM).

Yield: 18.3 mg (21.8 µmol, 35 %) of a red solid.

C₅₆H₄₂N₂O₆ [838.94]

¹H-NMR (600 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 9.65 \text{ (d, } {}^{3}J_{\text{HH}} = 8.3 \text{ Hz}, \text{ 1H} \text{)}, 9.63 \text{ (d, } {}^{3}J_{\text{HH}} = 8.3 \text{ Hz}, \text{ 1H} \text{)}, 8.64 \text{ (d, } {}^{3}J_{\text{HH}} = 8.3 \text{ Hz}, \\ & 1\text{H} \text{)}, 8.60 \text{ (d, } {}^{3}J_{\text{HH}} = 8.3 \text{ Hz}, \text{ 1H} \text{)}, 8.35 \text{ (s, 1H)}, 8.32 \text{ (s, 1H)}, 7.59 \text{ (d,} \\ & {}^{3}J_{\text{HH}} = 8.3 \text{ Hz}, \text{ 1H} \text{)}, 7.58 - 7.53 \text{ (m', 2H)}, 7.52 - 7.45 \text{ (m', 6H)}, 7.33 - 7.25 \text{ (m', 4H)}, 7.25 - 7.18 \text{ (m', 4H)}, 7.02 \text{ (d, } {}^{4}J_{\text{HH}} = 2.3 \text{ Hz}, \text{ 1H} \text{)}, 1.30 \text{ (s, 9H)}, 1.24 \text{ (s, 9H)}. \end{split}$$

¹³C-NMR (150 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 164.7 \ (\text{C}_{\text{q}}), 164.2 \ (\text{C}_{\text{q}}), 163.8 \ (\text{C}_{\text{q}}), 163.3 \ (\text{C}_{\text{q}}), 155.7 \ (\text{C}_{\text{q}}), 155.6 \ (\text{C}_{\text{q}}), 155.5 \ (\text{C}_{\text{q}}), \\ 155.3 \ (\text{C}_{\text{q}}), 150.8 \ (\text{C}_{\text{q}}), 144.5 \ (\text{C}_{\text{q}}), 135.8 \ (\text{C}_{\text{q}}), 134.03 \ (\text{C}_{\text{q}}), 133.99 \ (\text{C}_{\text{q}}), 133.4 \\ (\text{C}_{\text{q}}), 130.92 \ (\text{CH}), 130.88 \ (\text{CH}), 130.75 \ (\text{CH}), 130.67 \ (\text{CH}), 130.0 \ (\text{C}_{\text{q}}), 129.9 \\ (\text{C}_{\text{q}}), 129.7 \ (\text{CH}), 129.4 \ (\text{CH}), 129.4 \ (\text{CH}), 129.2 \ (\text{CH}), 129.10 \ (\text{CH}), 129.07 \\ (\text{CH}), 128.2 \ (\text{CH}), 126.5 \ (\text{CH}), 126.05 \ (\text{C}_{\text{q}}), 125.96 \ (\text{C}_{\text{q}}), 125.4 \ (\text{CH}), 125.3 \\ (\text{CH}), 125.03 \ (\text{C}_{\text{q}}), 124.99 \ (\text{CH}), 124.92 \ (\text{C}_{\text{q}}), 124.89 \ (\text{CH}), 124.8 \ (\text{C}_{\text{q}}), 124.5 \\ (\text{C}_{\text{q}}), 123.1 \ (\text{C}_{\text{q}}), 122.9 \ (\text{C}_{\text{q}}), 119.7 \ (\text{CH}), 119.5 \ (\text{CH}), 35.8 \ (\text{C}_{\text{q}}), 34.5 \ (\text{C}_{\text{q}}), 31.8 \\ (\text{CH}_{3}), 31.3 \ (\text{CH}_{3}). \end{split}$$

ESI-HR-MS (pos.):

calc.: [M+Na]⁺⁺ 861.2935 m/z

found: [M+Na]⁺ 861.2936 m/z

 $\Delta = 0.12 \text{ ppm}$

Synthesis of **PDI(SPh)**₂



Modified synthesis according to literature.^{2, 3}

Under a nitrogen atmosphere, **PDI(Br)**₂ (30.0 mg, 36.9 µmol), and potassium carbonate (30.6 mg, 221 µmol) were dissolved in dry, degassed toluene (4 mL). Then benzenethiol (0.1 mL, , 980 µmol) was added while stirring and the reaction mixture was stirred for 18 h at 65 °C. The mixture then was cooled down to room temperature and the solvent was removed *in vacuo*. The residue was dissolved in DCM and washed three times with water. The organic phase was dried over magnesium sulphate and the solvent was removed *in vacuo*. The crude product was purified via column chromatography (DCM) and via preparative thin layer chromatography (DCM).

Yield: 22.4 mg (25.7 μ mol, 70 %) of a purple solid.

C₅₆H₄₂N₂O₄S₂ [871.08]

¹**H-NMR** (600 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 8.88 \text{ (d, } ^{3}J_{\text{HH}} = 7.9 \text{ Hz}, \text{ 1H}), 8.84 \text{ (d, } ^{3}J_{\text{HH}} = 7.9 \text{ Hz}, \text{ 1H}), 8.77 \text{ (d, } ^{3}J_{\text{HH}} = 7.9 \text{ Hz}, \\ & 1\text{H}), 8.74 \text{ (d, } ^{3}J_{\text{HH}} = 7.9 \text{ Hz}, \text{ 1H}), 8.48 \text{ (s, } 1\text{H}), 8.42 \text{ (s, } 1\text{H}), 7.59 \text{ (d, } \\ & ^{3}J_{\text{HH}} = 8.6 \text{ Hz}, \text{ 1H}), 7.58 - 7.49 \text{ (m'}, \text{ 7H}), 7.48 \text{ (dd, }, ^{3}J_{\text{HH}} = 8.6 \text{ Hz}, ^{4}J_{\text{HH}} = 2.3 \text{ Hz}, \\ & 1\text{H}), 7.46 - 7.42 \text{ (m'}, 6\text{H}), 7.32 - 7.29 \text{ (m'}, 2\text{H}), 7.01 \text{ (d, } ^{4}J_{\text{HH}} = 2.2 \text{ Hz}, \text{ 1H}), 1.32 \\ & (\text{s, } 9\text{H}), 1.24 \text{ (s, } 9\text{H}). \end{split}$$

¹³C-NMR (150 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 164.8 \ (\text{C}_{\text{q}}), 164.4 \ (\text{C}_{\text{q}}), 163.8 \ (\text{C}_{\text{q}}), 150.7 \ (\text{C}_{\text{q}}), 144.5 \ (\text{C}_{\text{q}}), 139.2 \ (\text{C}_{\text{q}}), \\ & 139.0 \ (\text{C}_{\text{q}}), 135.8 \ (\text{C}_{\text{q}}), 134.5 \ (\text{CH}), 134.4 \ (\text{CH}), 134.2 \ (\text{CH}), 134.1 \ (2\times\text{CH}), \\ & 133.8 \ (\text{C}_{\text{q}}), 133.8 \ (\text{C}_{\text{q}}), 133.40 \ (\text{C}_{\text{q}}), 133.37 \ (\text{C}_{\text{q}}), 133.32 \ (\text{C}_{\text{q}}), 133.26 \ (\text{C}_{\text{q}}), 130.5 \ (\text{CH}), 130.4 \ (\text{CH}), 130.0 \ (\text{CH}), 129.91 \ (\text{CH}), 129.89 \ (\text{CH}), 129.85 \ (\text{CH}), 129.8 \ (\text{CH}), 129.7 \ (\text{CH}), 129.6 \ (\text{CH}), 129.2 \ (\text{CH}), 129.1 \ (\text{CH}), 129.0 \ (\text{C}_{\text{q}}), 128.1 \ (\text{CH}), \\ & 126.7 \ (\text{C}_{\text{q}}), 126.6 \ (\text{C}_{\text{q}}), 126.5 \ (\text{CH}), 123.1 \ (\text{C}_{\text{q}}), 122.9 \ (\text{C}_{\text{q}}), 122.7 \ (\text{C}_{\text{q}}), 122.4 \ (\text{C}_{\text{q}}), 35.8 \ (\text{C}_{\text{q}}), 34.5 \ (\text{C}_{\text{q}}), 31.8 \ (\text{CH}_3) \ 31.3 \ (\text{CH}_3). \end{split}$$

ESI-HR-MS (pos.):

calc.: [M+Na]⁺⁺ 893.2478 m/z

found: [M+Na]⁺ 893.2454 m/z

 $\Delta = 2.69 \text{ ppm}$

Synthesis of **PDI(SePh)**₂



Modified synthesis according to literature.^{2, 3}

Under a nitrogen atmosphere, **PDI(Br)**₂ (40.0 mg, 49.2 µmol), and potassium carbonate (40.8 mg, 295 µmol) were dissolved in dry, degassed toluene (5 mL). Then benzeneselenol (0.1 mL, 942 µmol) was added while stirring and the reaction mixture was stirred for 18 h at 65 °C. The mixture was then cooled down to room temperature and the solvent was removed *in vacuo*. The residue was dissolved in DCM and washed three times with water. The organic phase was dried over magnesium sulphate and the solvent was removed *in vacuo*. The crude product was purified via column chromatography (DCM) and via preparative thin layer chromatography (DCM).

Yield: 9.00 mg (9.33 µmol, 19 %) of a purple solid.

 $C_{56}H_{42}N_2O_4Se_2$ [964.86]

¹**H-NMR** (600 MHz, CD₂Cl₂):

 $\delta \text{ [ppm]} = 8.82 \text{ (d, } {}^{3}J_{\text{HH}} = 7.9 \text{ Hz, } 1\text{H} \text{), } 8.78 \text{ (d, } {}^{3}J_{\text{HH}} = 7.9 \text{ Hz, } 1\text{H} \text{), } 8.54 \text{ (s, } 1\text{H} \text{), } 8.50 \text{ (s, } 1\text{H} \text{), } 8.40 \text{ (d, } {}^{3}J_{\text{HH}} = 7.9 \text{ Hz, } 1\text{H} \text{), } 8.39 \text{ (d, } {}^{3}J_{\text{HH}} = 7.7 \text{ Hz, } 1\text{H} \text{), } 7.68 - 7.64 \text{ (m', } 1\text{ H)} \text{$

4H), 7.59 (d, ${}^{3}J_{HH}$ = 8.7 Hz, 1H), 7.58 – 7.54 (m', 2H), 7.52 – 7.49 (m', 4H), 7.44 – 7.40 (m', 4H), 7.32 – 7.29 (m', 2H), 7.01 (d, ${}^{4}J_{HH}$ = 2.2 Hz, 1H), 1.32 (s, 9H), 1.24 (s, 9H).

¹³C-NMR (150 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 164.8 \ (\text{C}_{\text{q}}), \ 164.5 \ (\text{C}_{\text{q}}), \ 163.9 \ (\text{C}_{\text{q}}), \ 163.6 \ (\text{C}_{\text{q}}), \ 150.7 \ (\text{C}_{\text{q}}), \ 144.5 \ (\text{C}_{\text{q}}), \ 136.31 \\ (\text{CH}), \ 136.26 \ (\text{C}_{\text{q}}), \ 136.23 \ (\text{C}_{\text{q}}), \ 136.20 \ (\text{CH}), \ 135.9 \ (\text{C}_{\text{q}}), \ 135.8 \ (\text{CH}), \ 135.6 \\ (\text{CH}), \ 135.01 \ (\text{C}_{\text{q}}), \ 135.00 \ (\text{C}_{\text{q}}), \ 134.11 \ (\text{C}_{\text{q}}), \ 134.10 \ (\text{C}_{\text{q}}), \ 133.4 \ (\text{C}_{\text{q}}), \ 130.78 \\ (\text{C}_{\text{q}}), \ 130.77 \ (\text{C}_{\text{q}}), \ 130.6 \ (\text{CH}), \ 130.5 \ (\text{CH}), \ 130.24 \ (\text{CH}), \ 130.20 \ (\text{CH}), \ 129.9 \\ (\text{CH}), \ 129.8 \ (\text{CH}), \ 129.6 \ (\text{CH}), \ 129.2 \ (\text{CH}), \ 129.1 \ (2\times\text{CH}), \ 128.8 \ (\text{C}_{\text{q}}), \ 128.7 \\ (\text{C}_{\text{q}}), \ 128.6 \ (\text{CH}), \ 128.5 \ (\text{CH}), \ 128.1 \ (\text{CH}), \ 127.0 \ (\text{C}_{\text{q}}), \ 126.8 \ (\text{C}_{\text{q}}), \ 126.5 \ (\text{CH}), \\ 123.3 \ (\text{C}_{\text{q}}), \ 123.1 \ (\text{C}_{\text{q}}), \ 122.3 \ (\text{C}_{\text{q}}), \ 35.8 \ (\text{C}_{\text{q}}), \ 34.5 \ (\text{C}_{\text{q}}), \ 31.8 \ (\text{CH}_3), \\ 31.3 \ (\text{CH}_3). \end{split}$$

ESI-HR-MS (pos.):

calc.: [M+Na]⁻⁺ 989.1382 m/z found: [M+Na]⁻⁺ 989.1377 m/z Δ = 0.51



Modified synthesis according to literature.⁴

Under a nitrogen atmosphere, sodium borohydride (1.79 mg, 47.3 μ mol) and diphenyl ditelluride (19.4 mg, 47.4 μ mol) were dissolved in freeze-pump-thaw degassed DMF (6.00 mL) and stirred for 2 h at 70 °C. **PDI(Br)**₂ (35.0 mg, 43.1 μ mol) was dissolved in freeze-pump-thaw degassed THF (3.00 mL) under a nitrogen atmosphere and was added to the reaction mixture. The reaction was stirred for 20 minutes at room temperature. After stirring, the mixture was cooled down to room temperature and the solvent was removed *in vacuo*. The crude product was purified with column chromatography (DCM).

Yield: 14.2 mg (13.4 µmol, 31 %) of a dark purple solid.

C₅₆H₄₂N₂O₄Te₂ [1062.15]

ESI-HR-MS (pos.):

calc.: [M+Na]^{.+} 861.2935 m/z

found:	[M+Na] [.]	+ 861.2936 m/z	$\Delta = -0.54$
ound.		001.2000 m/2	- 0.0+

¹H-NMR (400 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 8.85 \text{ (d, } ^{3}J_{\text{HH}} = 7.8 \text{ Hz}, \text{ 1H}), \ 8.82 \text{ (d, } ^{3}J_{\text{HH}} = 7.8 \text{ Hz}, \text{ 1H}), \ 8.71 \text{ (s, 1H)}, \ 8.70 \text{ (s,} \\ & 1\text{H}), \ 7.94 - 7.90 \text{ (m', 4H)}, \ 7.88 \text{ (d, } ^{3}J_{\text{HH}} = 8.0 \text{ Hz}, \text{ 1H}), \ 7.87 \text{ (d, } ^{3}J_{\text{HH}} = 7.9 \text{ Hz}, \\ & 1\text{H}), \ 7.60 - 7.46 \text{ (m', 7H)}, \ 7.40 - 7.34 \text{ (m', 4H)}, \ 7.32 - 7.27 \text{ (m', 2H)}, \ 7.01 \text{ (d,} \\ & ^{4}J_{\text{HH}} = 2.2 \text{ Hz}, \ 1\text{H}), \ 1.32 \text{ (s, 9H)}, \ 1.23 \text{ (s, 9H)}. \end{split}$$

¹³C-NMR (100 MHz, CD₂Cl₂):

$$\begin{split} \delta \text{ [ppm]} = & 164.8 \ (\text{C}_{\text{q}}), \ 164.6 \ (\text{C}_{\text{q}}), \ 163.9 \ (\text{C}_{\text{q}}), \ 163.7 \ (\text{C}_{\text{q}}), \ 150.7 \ (\text{C}_{\text{q}}), \ 144.5 \ (\text{C}_{\text{q}}), \ 140.8 \\ (\text{CH}), \ 140.7 \ (\text{CH}), \ 139.7 \ (\text{CH}), \ 139.4 \ (\text{CH}), \ 139.2 \ (\text{C}_{\text{q}}), \ 139.1 \ (\text{C}_{\text{q}}), \ 135.9 \ (\text{C}_{\text{q}}), \\ & 135.61 \ (\text{C}_{\text{q}}), \ 135.58 \ (\text{C}_{\text{q}}), \ 133.5 \ (\text{C}_{\text{q}}), \ 130.61 \ (\text{CH}), \ 130.56 \ (\text{CH}), \ 130.42 \ (\text{CH}), \\ & 130.39 \ (\text{CH}), \ 130.3 \ (\text{CH}), \ 130.2 \ (\text{CH}), \ 129.6 \ (\text{CH}), \ 129.2 \ (\text{CH}), \ 129.10 \ (\text{CH}), \\ & 129.08 \ (\text{CH}), \ 128.3 \ (\text{C}_{\text{q}}), \ 128.2 \ (\text{C}_{\text{q}}), \ 128.1 \ (\text{CH}), \ 127.5 \ (\text{C}_{\text{q}}), \ 123.3 \ (\text{C}_{\text{q}}), \\ & (\text{CH}), \ 127.4 \ (\text{CH}), \ 126.5 \ (\text{CH}), \ 126.1 \ (\text{CH}), \ 123.5 \ (\text{C}_{\text{q}}), \ 123.3 \ (\text{C}_{\text{q}}), \end{split}$$

122.3 (C_q), 122.2 (C_q), 121.9 (C_q), 121.7 (C_q),118.3 (C_q), 118.2 (C_q), 35.8 (C_q), 34.5 (C_q), 31.8 (CH₃), 31.3 (CH₃).



Figure S 3: ¹³C-NMR of (2) in CDCl₃ (100 MHz).



Figure S 5: 13 C-NMR of (3) in CDCl₃ (100 MHz).



Figure S 7: ¹³C-NMR of PDI(Br)₂ in CDCI₃ (100 MHz).



Figure S 9: ¹³C-NMR of PDI(OPh)₂ in CDCI₃ (150 MHz).



Figure S 11: ¹³C-NMR of PDI(SPh)₂ in CD₂Cl₂ (150 MHz).



Figure S 13: ¹³C-NMR of PDI(SePh)₂ in CD₂Cl₂ (150 MHz).

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Figure S 15: ¹³C-NMR of PDI(TePh)₂ in CD₂Cl₂ (100 MHz).

3 Steady State Absorption and Emission Spectroscopy

The used toluene had spectroscopic grade and was used as received without any further purification (Acros Organics, Supelco).

Absorption spectroscopy

- Jasco V670 UV/vis/NIR spectrophotometer (software: SpectraManager v.2.08.04)
- Agilent Technologies Cary 5000 UV/vis/NIR spectrophotometer (software: Agilent Cary

WinUV Analysis and Bio v.4.2)

Absorption measurements were carried out in quartz cuvettes from Starna (10 mm, Pfungstadt, Germany) at rt. The aggregation of the compounds could be excluded by measuring samples with different concentrations ($10^{-7} - 10^{-5}$ M).

Emission spectroscopy

Edinburgh Instruments FLS980 fluorescence lifetime spectrometer

- Software F980 v.1.4.5
- 450 W continuous xenon arc lamp
- Double excitation and emission monochromator
- PMT (R928P for 300-800 nm, R5509-42 for 700-1200 nm)

Emission spectra were recorded with diluted samples ($OD_{max} < 0.05$) to avoid self-absorption effects. Absolute fluorescence quantum yields were determined with an integrating sphere and Eq. S1:

$$\phi_{\text{meas}} = \frac{\int F_{\text{sample}}}{\int E_{\text{solvent}} - \int E_{\text{sample}}}$$
S1

Here, ϕ_{obs} is the measured quantum yield, F_{sample} is the emission spectrum of the sample, E_{sample} is the spectrum of the excitation light with a sample and $E_{solvent}$ is the spectrum of the excitation light with a blank sample. The measured absolute quantum yields were corrected for self-absorption using the method of Bardeen et al.⁵

The singlet oxygen quantum yield of **PDI(SePh)**₂ was determined in an air-purged DCM solution (OD_{596nm} = 0.324) as an average of four independent measurements. Methylene Blue was used as the reference (Φ_{Δ} = 0.57 in DCM)⁶. Both solutions (sample and reference) were excited at 16800 cm⁻¹ (596 nm) and the singlet oxygen emission was detected between

8130 cm⁻¹ (1230 nm) and 7580 cm⁻¹ (1320 nm) with a 850 nm longpass filter in the emission arm of the FLS980.

For time dependent emission spectroscopy, the same spectrometer was used.

- Pulsed laser diode (PLD): 19700 cm⁻¹ (508 nm)
- PMT (H10720-01)
- Software: FAST v.3.4.2



Figure S 16: a) Emission of **PDI(OPh)**₂ in toluene at rt and 77K¹, b) emission of **PDI(SPh)**₂ in toluene at rt and 77K, c - e) solvent dependent emission spectra of **PDI(XPh)**₂ (X = O, S, Se) and f) singlet oxygen emission of **PDI(SePh)**₂ in DCM referenced against Methylene Blue.

¹ Because of the small stokes shift, self-absorption couldn't be avoided, so the main emission band is distorted.

4 fs-Transient Absorption Spectroscopy and Fluorescence Upconversion

The TA setup is based on a HELIOS transient absorption spectrometer (TAS) from Ultrafast Systems. The whole setup is described in Auerhammer et al.⁷ The Helios TAS consists of two fibre-coupled, linear CMOS sensors with a sensitivity from 315 nm to 925 nm for the measurement and reference channel. The probe wavelength range was set with a 400 nm longpass filter and a BG38 filter from 400 nm to 800 nm. The whitelight continuum (WLC) is created by an oscillating, 3 mm thick CaF₂ crystal which is pumped with ca. 2 uJ at 800 nm. The pump beam for the WLC is guided over a linear stage which provides a time delay up to 7 ns. The angle between pump and probe beam is ca. 10° and the angle between the polarization directions is 54.7° (magic angle conditions). The pump beam was produced from a laboratory-constructed NOPA at the specified wavelengths. The pulse lengths are shorter than 30 fs at all three pump wavelengths and they were close to the bandwidth limitation. The instrument response function is ca. 60 fs which was derived from the coherent artifact. The whole setup is driven by a one-box femtosecond laser system "Solstice" from Newport Spectra Physics. The fundamental wavelength is 800 nm with a repetition rate of 1 kHz and a pulse length of 100 fs. All samples were dissolved in toluene and measured in a 0.2 mm cuvette. **PDI(OPh)**₂ was pumped at $\lambda = 538$ nm with pulse power (pp) = 30 nJ and an absorbance A = 0.19 (**PDI(SPh)**₂: λ = 556 nm, pp = 30 nJ, A = 0.10; **PDI(SePh)**₂: λ = 556 nm, pp = 30 nJ, A = 0.23; **PDI(TePh)**₂: λ = 587 nm, pp = 20 nJ, A = 0.12).

Broadband Fluorescence Upconversion Spectrometer (FLUPS): The FLUPS is a commercially available broadband fluorescence upconversion spectrometer kit from LIOPTEC which provides a measuring range from 395 - 850 nm of fluorescence. The whole setup is described in Hattori et al.⁸ The laser source is a "Solstice" from Newport Spectra Physics with a fundamental wavelength of 800 nm and a repetition rate of 1 kHz. The FLUPS itself was driven by two NOPAs from which one provides the gate pulse of 1280 nm with 40 μ J and the other one provides the excitation pulses of 490 nm and 530 nm with 400 μ J. The achieved instrumental response function was estimated to 240 fs with GLOTARAN. The samples were dissolved in spectroscopic grade toluene from Thermo Scientific and filled into a fused silica cuvette with an optical path length of 1 mm. The absorbance of **PDI(OPh)**₂ at the excitation wavelength 490 nm was set to 0.16 and of **PDI(SPh)**₂ at 530 nm to 0.15. To cut off the excitation pulse after the fluorescence in case of **PDI(OPh)**₂ a dielectric long pass filter with 500 nm was used and for the **PDI(SPh)**₂ a 550 nm filter, respectively.









Figure S 17: a-h) Chirp corrected fs-transient absorption data for PDI(XPh)₂ in toluene. Early spectra are depicted in purple, later times in red and i-j) deconvoluted fluorescence upconversion spectra of PDI(OPh)₂ and PDI(SPh)₂ in toluene.

5 ns-Transient Absorption Spectroscopy

- Ediburgh LP920 laser flash spectrometer with a 450 Xe arc lamp
- PMT (Hamamatsu R955)
- Digital Storage Oscilloscope (Tektronix TD3012B)
- L900 software (v. 7.3.5)
- EKSPLA NT340 Nd:YAG laser with OPO
- Continuum Minilite II Nd:YAG

The setup for the ns-transient absorption spectroscopy is based on an Edinburgh LP920 laser flash spectrometer. As the excitation light source, an EKSPLA NT340 Nd:YAG laser with an integrated optical parametric oscillator (400-800 nm) or a Continuum Minilite II Nd:YAG (355 nm) was used, both operating at a repetition rate of 10 Hz. The white light for the probe pulse was generated by a 450 W Xe arc flash lamp and was perpendicular to the excitation light.

The used toluene had spectroscopic grade (Acros Organics, Supelco) and was degassed by five freeze-pump-thaw cycles. Sample preparation was done in a nitrogen filled glove-box in a 10 mm x 10 mm quartz-cuvette (Starna, Pfungstadt, Germany) equipped with a Young's valve. The samples had an optical density of about 0.3 at the excitation wavelength and were excited with ca. 5 ns laser pulses at their lower energy absorption maximum.

For the sensitizing experiments with $PDI(OPh)_2$ and $PDI(SPh)_2$, samples with an optical density of about 0.7 were used and anthracene was added (optical density of the anthracene absorption maximum was ca. 0.4). Here, anthracene was excited with a 28200 cm⁻¹ (355 nm) laser pulse from the Continuum Minilite laser. Transient maps were obtained by measuring temporal decay profiles in 4 nm steps from 25000 cm⁻¹ (400 nm) to 12500 cm⁻¹ (800 nm) and corrected for fluorescence with the software fluorescence correction.



2000 t/μs

3000

4000

0.0

0

1000



-0.050 170 ns 14000 16000 18000 20000 22000 24000 *i*⁄/ cm¹ **Figure S 18:**). Fit for the respective lifetimes of the anthracene sensitized triplet states of a) **PDI(OPh)**₂ and b) **PDI(SPh)**₂, ns-TA spectra of **PDI(SPh)**₂ without sensitizer (c and d), of e) **PDI(SePh)**₂ and f) **PDI(TePh)**₂ and g) the decay curves of the deaerated and aerated solution of **PDI(SePh)**₂. All measurements were performed in toluene.

6 Electrochemical Measurements

- Gamry Instruments Reference 600 Potentiostat/Galvanostat (v.6.2.2.)
- Platinum Disc Working Electrode (Ø = 1 mm)
- Platinum Wire Counter Electrode
- Platinum Pseudo Reference Electrode

Cyclic voltammetric measurements were performed with a three electrode setup and referenced against ferrocene/ferrocenium. SEC measurements were performed on the aforementioned Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer under an argon atmosphere in DCM in a custom-built three electrode quartz-cell in reflection mode. The cell consisted of a platinum disc working electrode ($\emptyset = 6$ mm), a platinum plate counter electrode ($\emptyset = 1$ mm) and an Ag/AgCl pseudo-reference electrode. The path length was 100 µm.





Figure S 19: a) Cyclic voltammograms of **PDI(XPh)**₂ (DCM, TBAHF 0.2 M, 100 mV s⁻¹) and b - g).absorption spectra of mono and double reduced species of **PDI(XPh)**₂ for X = O, S, Se.

7 EPR

EPR measurements at X-band (9.38 GHz) were performed using a Bruker ELEXSYS E580 CW EPR spectrometer equipped with an Oxford Instruments helium cryostat (ESR900) and a MercuryiTC temperature controller. The spectral simulations were performed using the Easyspin 5.2.28 Toolbox⁹ and MATLAB 9.7 (R2019b).



Figure S 20: EPR-simulations with the second derivative of the signal for a) $PDI(OPh)_2$ and b) $PDI(SePh)_2$ and c – f) EPR-simulations of frozen solutions for anisotropic *g*-factors.

	PDI(OPh)2 ⁻	PDI(SPh)2 ⁻	PDI(SePh) ₂ -	PDI(TePh) ₂ -
$g_{iso}(rt)$	2.0030	2.0036	2.0043	2.0045
g _{iso} (77K)	2.00217	2.00232	2.00276	2.00268
g _{zz} (77K)	2.00326	2.00380	2.00467	2.00847
g _{уу} (77К)	2.00264	2.00257	2.00334	2.00272
g _{xx} (77K)	2.00062	2.00060	2.00028	1.99685

Table S 1: Experimental isotropic and anisotropic *g*-factors of **PDI(XPh)**₂⁻ determined at X-Band at rt and at 77K.

8 TD-DFT calculations

All quantumchemical calculations were performed with two identical phenyl rings at the imide positions instead of two different ones.

All structures were optimized using Gaussian 09 at the (U)B3LYP level of theory and a def2-SVP basis set for the oxygen and tellurium compound (S_0 , S_1 and T_1 state) and for the sulphur and selenium compounds (S_0 state). The S_1 and T_1 geometries for the sulphur compound were optimized with a def2-SVP basis set for the CHNO atoms and a def2-QZVP basis set for the S atoms. The S_1 and T_1 geometries for the selenium compound were optimized with a def2-SVP basis set for the selenium compound were optimized with a def2-SVP basis set for the selenium compound were optimized with a def2-SVP basis set for the selenium compound were optimized with a def2-SVP basis set for the selenium compound were optimized with a def2-SVP basis set for the S atoms. The S₁ and T₁ geometries for the selenium compound were optimized with a def2-SVP basis set for the CHNO atoms and a def2-TZVP basis set for the S atoms. All anionic geometries were optimized using uB3LYP/def2-SVP.

The TD-DFT calculations were performed using ORCA 5.0.3 at the (U)B3LYP level of theory, applying a zero-order regular approximation. The calculations of all compounds (both neutral and anionic) were performed with a ZORA-def2-TZVP SARC/J basis set. For selenium, an additional ZORA-TZVP basis and for tellurium, an additional SARC-ZORA-TZVP basis set was used. Spin-orbit coupling matrix elements were calculated with the mean-field/effective potential operator at B3LYP/ZORA-def2-TZVP.

	$S_1 \leftarrow S_0 \ / \ cm^{-1}$	f	$S_2 \leftarrow S_0 \ / \ cm^{-1}$	f	$S_3 \leftarrow S_0 / \text{ cm}^-$	f
PDI(OPh) ₂	20036	1.045	24124	0.005	24357	0.142
PDI(SPh) ₂	18782	0.807	22490.	0.024	23287	0.331
PDI(SePh) ₂	18194	0.665	21166	0.023	22766	0.440
PDI(TePh) ₂	16731	0.437	18650	0.020	21768	0.583

Table S 2: TD-DFT calculated transitions of PDI(XPh)₂ at B3LYP/def2-TZVP.

Table S 3: TD-DFT calculated transitions^a of PDI(XPh)₂⁻ at B3LYP/def2-TZVP.

	$D_1 \leftarrow D_0 \ / \ cm^{-1}$	f	$D_2 \leftarrow D_0 \ / \ cm^{-1}$	f	$D_3 \leftarrow D_0 / \text{ cm}^{-1}$	f
PDI(OPh)2 ⁻	11861	0.0004	13850	0.0552	17833	1.0294
PDI(SPh)2 ⁻	12140	0.0007	14129	0.0506	17143	0.6607
PDI(SePh) ₂ -	11866	0.0009	13954	0.0537	16964	0.7166
PDI(TePh)₂ ⁻	11752	0.0008	14039	0.0559	16266	0.2024
	F : 44					

^aNot shifted, see Fig. 11.

HOMO and LUMO plots (B3LYP/def2TZVP)

PDI(OPh)₂









HOMO (-5.7960 eV)



LUMO (-3.4069 eV)



S₀ LUMO+1 (-2.0164 eV)



S₁

PDI(SPh)₂









HOMO (-5.7906 eV)



LUMO (- 3.4232)



S₀ LUMO+1 (-2.0245 eV)







HOMO (-5.6817 eV)



LUMO (-3.8912 eV)



S₁ LUMO+1 (-2.2477 eV)



Figure S 24: HOMO and LUMO plots of PDI(TePh)2.

Computational details of DFT g-tensor computations

Using the B3LYP/def2-SVP optimized structures of the radical anions, EPR g-tensors have been carried out with a release candidate of the Turbomole 7.7 package,^{10, 11} using the converged one-component (1c) scalar relativistic and two-component (2c) spin-orbit coupled wavefunctions obtained with the ridft module. In the former case, the SOC effects are incorporated perturbationally. We evaluated the BP86¹²⁻¹⁴ and B3LYP^{15, 16} functionals and report only the B3LYP results in the main text. The quasirelativistic exact two-component^{17, 18} (X2C) Hamiltonian was used with a finite nucleus model together with the diagonal local approximation (DLU) to the unitary decoupling transformation.^{19, 20} These calculations used gauge-including atomic orbitals (GIAOs²¹) to deal with the gauge-dependence of the external magnetic vector potential. In case of the 2c calculations we report also below results obtained with a common gauge origin (CGO) at the heaviest atom of the given radical to estimate the importance of gauge effects. Two-electron spin-orbit coupling contributions have been modeled with Böttger's modified screened-nuclear spin-orbit (mSNSO) approximation.^{22, 23} x2c-TZVPall-2c²⁴ basis sets, the RI approximation to the Coulomb integrals, and gridsize 3a have been used. The CGO calculations were obtained as an expectation value within the ridft module. The GIAO calculations were obtained with Franzke's very recent implementation in the mpshift module.²⁵ The derivatives of the decoupling and the renormalization matrices to X2C²⁵ were included in all calculations.

	PDI(OPh)2 ⁻				PDI(SPh)2 ⁻			PDI(SePh)	2	PDI(TePh)2 ⁻			
	exp	BP86	B3LYP	exp	BP86	B3LYP	exp	BP86	B3LYP	exp	BP86	B3LYP	
\boldsymbol{g}_{yy}	2.00326	2.003068	2.003313	2.00380	2.002979	2.003122	2.00467	2.006031	2.006013	2.00847	2.011537	2.01075	
g _{xx}	2.00264	2.002754	2.002722	2.00257	2.002747	2.002781	2.00334	2.003884	2.003651	2.00272	2.004021	2.00274	
g _{zz}	2.00062	2.000657	2.000653	2.00060	2.000102	2.000117	2.00028	1.997261	1.997521	1.99685	1.992242	1.99376	
\boldsymbol{g}_{iso}	2.00217	2.002160	2.002229	2.00232	2.001943	2.002007	2.00276	2.002392	2.002395	2.00268	2.002600	2.00242	
a CGC	$^{\circ}$ CGO stands for a common gauge origin of the magnetic vector potential at the heaviest atom of the radical												

^a CGO stands for a common gauge origin of the magnetic vector potential at the heaviest atom of the radical.

Table S5: Experimental (X-band at 77K) and computed (2c-X2C-mSNSO/BP86/x2c-TZVPall-2c) *g*-tensors of **PDI(XPh)**₂⁻.

	PDI(OPh)2 ⁻			PDI(SPh)2 ⁻			PDI(SePh)2 ⁻			PDI(TePh)2 ⁻			
	exp	CGO*	GIAO	exp	CGOª	GIAO	exp	CGO ^a	GIAO	exp	CGO ^a	GIAO	
g _{yy}	2.00326	2.003623	2.002956	2.00380	2.003390	2.002940	2.00467	2.006378	2.006008	2.00847	2.010579	2.010171	
g _{xx}	2.00264	2.002663	2.002665	2.00257	2.002559	2.002704	2.00334	2.003915	2.003923	2.00272	2.003008	2.003151	
g _{zz}	2.00062	2.000324	2.000513	2.00060	2.000039	2.000006	2.00028	1.997159	1.997087	1.99685	1.989956	1.989687	
g iso	2.00217	2.002203	2.002045	2.00232	2.001996	2.001883	2.002763	2.002484	2.002339	2.00268	2.001181	2.001003	
a CCO	stands for	a common o		of the mean	otic voctor p	otoptial at the	o hooviast at	om of the rea	dical				

^a CGO stands for a common gauge origin of the magnetic vector potential at the heaviest atom of the radical.

Table S6: Experimental (X-band at 77K) and computed (2c-X2C-mSNSO/B3LYP/x2c-TZVPall-2c) *g*-tensors of **PDI(XPh)**₂⁻.

	PDI(OPh)2 ⁻				PDI(SPh)2 ⁻			PDI(SePh)2		PDI(TePh) ₂ .			
	exp	CGO ^a	GIAO	exp	CGOª	GIAO	exp	CGO ^a	GIAO	exp	CGO ^a	GIAO	
\boldsymbol{g}_{yy}	2.00326	2.003703	2.003186	2.00380	2.003351	2.003050	2.00467	2.006280	2.005991	2.00847	2.010212	2.009842	
g _{xx}	2.00264	2.002824	2.002624	2.00257	2.002718	2.002716	2.00334	2.003790	2.003711	2.00272	2.002140	2.002228	
g _{zz}	2.00062	2.000274	2.000521	2.00060	2.000068	2.000049	2.00028	1.997470	1.997400	1.99685	1.992018	1.991750	
\boldsymbol{g}_{iso}	2.00217	2.002267	2.002110	2.0023	2.002046	2.001938	2.002763	2.002513	2.002367	2.00268	2.001457	2.001273	
• ~ ~ ~									ما الم ما				

^a CGO stands for a common gauge origin of the magnetic vector potential at the heaviest atom of the radical.



Figure S25: Orientation of the computed *g*-tensor components relative to the PDI molecular frame for the example of **PDI(TePh)**₂⁻ (2c-X2C-mSNSO-GIAO/B3LYP/x2c-TZVPall-2c)



Figure S26: Computed spin-density distribution (+/-0.001 a.u. isosurfaces) for the example of **PDI(SePh)**₂⁻ (1c-X2C-B3LYP/x2c-TZVPall-2c).

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