Supporting Informations

New sulfonated perylene diimide pyrazolate ligands: a simple route

toward n-type redox-active hybrid materials

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General methods and apparatus

General methods:

All aqueous solutions were prepared with Milli-Q water. Unless otherwise indicated, all other reagents are commercially purchased from Sigma-Aldrich, Alfa Aesar, Fisher Scientific or VWR (Germany) and used as received. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out with Merck 5735 Kieselgel 60F254. (0.040-0.063 nm mesh).

Characterisations:

¹H and ¹³C NMR spectra were recorded on an *AVANCE 300 MHz BRUKER, AVANCE III 400 MHZ BRUKER*, chemical shifts for ¹H NMR spectra were calibrated on residual protons in the deuterated solvent (CDCl₃ δ = 7.26 ppm for ¹H and δ = 77.16 ppm for ¹³C ; d⁸-THF δ = 3.57, 1.72 ppm for ¹H and δ = 25.4, 67.6 ppm for ¹³C ; MeOD δ = 3.31 ppm for ¹H and δ = 49.00 ppm for ¹³C; d⁶-DMSO δ = 2.50 ppm for ¹H and δ = 39.52 ppm for ¹³C; d¹-TFA δ = 11.50 ppm for ¹H and δ = 116.5 ppm for ¹³C) or on an internal reference (TMS, δ = 0 ppm for both ¹H and ¹³C). Spectra were recorded at room temperature; chemical shifts are given in ppm and coupling constants in Hz.

High-resolution mass spectra (HRMS) were obtained by electrospray ionization coupled with high resolution ion trap orbitrap (LTQ-Orbitrap, ThermoFisher Scientific) working in ion-positive or ion-negative mode.

Electrochemistry and UV-vis Spectrometry:

Electrochemical measurements were performed with a potentiostat-galvanostat *Autolab PGSTAT 302N* controlled by NOVA software using a conventional single-compartment three-electrode cell. The working electrode was made out of platinum mesh. A platinum disk electrode was used as a counter electrode and the reference one was saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was a solution at 0.1M tetrabutylammonium hexafluorophosphate in DMF and solution were purged with argon before measurements. Every experiment were conducted with a scan rate of 100 mV/s.

UV-visible absorption spectra in solution state were recorded at room temperature on a UV-2401PC Shimadzu spectrophotometer using 1 cm path length quartz cells. Every UV-Vis measurement was performed in THF/[HCl aq. 2M] 9:1

Emission spectra in solution state were recorded on a SPEX Fluoromax-4 Jobin Yvon fluorimeter (1 cm quartz cells).

The spectroelectrochemical measurements were conducted using the aforementioned i) potentiostatgalvanostat *Autolab PGSTAT 302N* controlled by NOVA software and ii) UV-2401PC Shimadzu spectrophotometer using. A compact one cell — three electrodes setup was used, consisting of a dedicated thin layer quartz cell (optical path of 0.5 mm), a platinum Gauze working electrode (80 mesh), a platinum wire counter electrode and a small Ag/AgNO₃ counter electrode, filled with a commercial electrolyte of tetrabutylammonium perchlorate 0.1M, silver nitrate 0.01M in ACN. The three electrodes, as well as a dedicated PTFE purging tube were held together in place by a PTFE cap. The aforementioned setup was purchased to BioLogic. The spectra were recorded by applying potential steps of 30 seconds, recording a UV-vis absorbance spectrum at the middle of every step, sufficient to reach a stationary regime. Every step was of increasingly cathodic potential, shifted from the previous by 0.05 V. The starting and ending potentials were chosen to be before the beginning of the first DPV wave and after the end of the second DPV wave ($i_c \approx 0 \mu A$), respectively.

Computational chemistry:

All calculations were performed with Gaussian16¹, using default procedures. Considering the strong electronic decorrelation between the π -conjugated core and the imide *N*-substituent (see **Figure S3**), we replaced the pyrazole moiety by a H-group, saving time and resources. We have used the M062X² hybrid functional together with the 6-31+G(d) basis set to optimize of geometry of the ground state. The applied thresholds for energy determination convergence and geometry optimization were of 10⁻¹⁰ a.u. and *"tight"*, respectively. The DFT integration grid was the so-called *"ultrafine grid"*. Computing the Hessian at the same level of theory allowed to verify the absence of imaginary frequencies and getting access to the free energies (G). The excited-state calculations for the determination of the SOMO energies of the radical anions were performed with TD-DFT determined with the $\omega\beta$ 97XD³ long-range corrected exchange-correlation functional combined to the wider 6-311++G(2df,2p) basis set. The solvent effects were estimated using the Polarizable Continuum Model (PCM) for THF. Every PDI was optimized at the D2 point group symmetry. Details about conformers and additional results can be found in the dedicated section of these Supplementary Informations.

Synthesis

Synthesis of 1: 1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxybisanhydride was synthetized according to the reported procedure of Jager *et al.*

Synthesis of 2: Dimethylpyrazole (7.0 g, 72.8 mmol) was dissolved in concentrated sulfuric acid (60 mL). The resulting colorless solution was stirred at room temperature and KNO_3 (12.8g, 126.6 mmol, 1.75eq) was added in one portion. Temperature was

raised to 110°C and the medium was stirred mildly for 16h. Eventually, the solution was brought back to room temperature and dropped on crushed ice. The resulting solution was slowly basified up to pH = 3, which resulted in the precipitation of the desired product **2** as a white solid. This solid was recovered by filtration and generously washed with distilled water. The drying process was sped up by dissolving **2** in ethyl acetate, drying this solution over MgSO₄ and evacuating the solvent under reduced pressure, resulting in **2** as dry white fluffy solid (9.4g, 91%).

HRMS ESI+ [M+H⁺] m/z calculated 142.0617; found 142.0620

NMR (¹H, MeOD, 300 MHz) δ (ppm) 2.51 (s) ; (¹³C, MeOD, 400MHz) δ (ppm) 12.87, 131.90

Synthesis of 3: 2 (9.2g, 64.8 mmol) was dissolved in methanol (650 mL) at room temperature. The resulting colorless solution was exposed to light vacuum, alternated with argon atmosphere, for a total of 3 vacuum/argon cycles. Palladium on carbon

N-NH V NH₂

N-NH

 NO_2

 $(0.92g, 10\%_W)$ was then added quickly and the atmosphere was again exchanged for argon. The same process was applied to exchange argon for hydrogen gas. The resulting dark suspension was left stirring vigorously at room temperature for 60h. Eventually, the medium was directly filtered through a celite pad, followed by a filtration over a silica pad (100% methanol). The now crystal clear solution was evacuated under reduced pressure, giving **3** as an off white product (6.77g, 94%).

HRMS ESI+ [M+H⁺] m/z calculated 112.0875; found 112.0879
NMR (¹H, MeOD, 300 MHz) δ (ppm) 2.14 (s) ; (¹³C, MeOD, 400MHz) δ (ppm) 9.46, 123.15

Synthesis of 4: 1 (0.5 g, 943 μ mol) and 3 (0.418 g, 3.77 mmol, 4.0eq) were suspended in propionic acid (36,5 mL). The reactive mixture was heated at 140°C for 2h. Eventually, water (60 mL) was added and the resulting reddish suspension was filtered. After several water washing, **4** was afforded as a red powder (0.660 g, 98%).



Synthesis of 5: 4 (0.100 g, 140 μmol), 18-C-6 (0.740 g, 5.6 mmol, 40eq), KF (0.162 g, 2.8 mmol, 20eq) were suspended/dissolved in THF (12 mL), in a sealable tube under Ar atm. The resulting red suspension turned purple upon addition of PrSH (0.25 mL, 2.8 mmol, 20eq). The tube was then sealed and the reactive mixture was heated at 74°C, under strong stirring, for 3h30. Eventually, water (20 mL) was added and the purple suspension was filtered. Chromatography column (silica gel, liquid deposition, dichloromethane, gradient methanol (0%-6%)) afforded **4** as a purple powder (0.112 g, 92%) **HRMS** ESI+ [M+H⁺] m/z calculated 875.2542; found 875.2515



NMR (¹H, CDCl₃, 400 MHz) δ (ppm) 8.77 (s, 4H), 3.01 (t, 8H), 2.20 (s, 12H), 1.56 (m, 8H), 0.91 (t, 12H); (¹³C, CDCl₃, 400MHz) δ (ppm) 139.49, 131.51, 131.24, 129.17, 122.67, 121.25, 40.75, 38.64, 31.93, 29.67, 29.64, 29.58, 29.42, 29.37, 28.24, 27.20, 22.70, 22.32, 14.13, 13.39

Synthesis of 6: 5 (0.120 g, 137 μ mol), di-*tert*-butyl dicarbonate (77 mg, 351 μ mol, 2.5 eq) and N,N'-dimethylaminopyridine (3.6 mg, 29 μ mol, 0.2 eq) were mixed in a flame-dried pyrex tube, under argon atmosphere. THF (2.4 mL) was added. The resulting dark purple solution was further added of triethylamine (30 μ L) and left stirring at room temperature for 1h. Eventually, 15 mL of cyclohexane were added and the resulting solution was directly deposited on top of a chromatography column (silica gel, cyclohexane). A full volume of cyclohexane was passed through, followed by THF, effectively eluting the product. The recovered fraction was evacuated under reduced pressure. The resulting dark purple sticky solid was dispersed by sonication in methanol and recovered by vacuum filtration, affording pure **6** (0.145 g, 98%) as a purple shiny powder.

HRMS ESI- [M⁻] m/z calculated 1074.3512; found 1074.3499

NMR (¹H, CDCl₃, 400 MHz) δ (ppm) 8.76 (s, 4H), 3.02 (m, 8H), 2.40 (s, 6H), 2.20 (s, 6H), 1.69 (s, 18H), 1.57 (m, 8H), 0.91 (t, J=7.30 Hz, 12H); (¹³C, CDCl₃, 400MHz) δ (ppm) 162.82, 149.60, 148.48, 141.15, 140.12, 131.66, 131.56, 129.64, 122.96, 120.86, 117.52, 85.31, 38.47, 38.38, 29.68, 28.05, 22.36, 13.46, 12.73, 11.96

Synthesis of 7: 6 (0.061 g, 57.1 µmol) was dissolved in dichloromethane (10 mL). The resulting dark purple solution was stirred gently and brought to 0°C and added of *meta*-chloroperoxybenzoic acid (1.05 g, 5.71 mmol, 100 eq) in one portion. The medium was shielded from light and left stirring in the ice bath, warming up progressively over 17h. Eventually, trifluoroacetic acid (0.5 mL) was added in the redish pink solution. After 1h of stirring at room temperature, solvents were evacuated under reduced pressure at 25°C. The resulting deposit was taken in diethyl ether (100 mL), sonicated 20min and



filtered to recover a partially cleaned solid. This solid was dissolved in a minimal amount of DCM/MeOH mixture (95:5) and purified with a chromatography column (silica gel, liquid deposition, DCM/MeOH 95:5). The product fractions were combined and evacuated under reduced pressure. The resulting sticky solid was sonicated in diethyl ether and filtered again, affording pure **7** (0.048 g, 83%) as a dark pink shiny powder.

HRMS ESI– [M-H⁻] m/z calculated 1003.2135; found 1003.2147

NMR (¹H, *d*⁸-THF, 400 MHz) δ (ppm) 9.10 (s, 4H), 3.49 (m, 4H), 3.17 (m, 4H), 2.10 (s, 12H), 1.63 (m, 4H), 1.45 (m, 4H), 0.85 (t, J=7.40 Hz, 12H); (¹³C, *d*¹-TFA, 400MHz) δ (ppm) 150.33, 149.85, 145.47, 145.11, 131.43, 128.52, 123.82, 69.18, 58.29, 14.91, 10.75, 8.10

Synthesis of 8: 4 (0.300 g, 419 μ mol) was exposed to high vacuum in a flame-dried pyrex tube, for 30 min. di-tert-butyl dicarbonate (0.365 g, 1.67 mmol, 4 eq) and dimethylaminopyridine (0.010 g, 83.7 μ mol, 0.2 eq) were then added under argon atmosphere. Dry dimethylformamide (20 mL) was then added and the resulting orange suspension was then stirred gently under argon at room temperature for 35 min. Eventually, the now yellow-emitting deep orange solution was added of dichloromethane (100 mL) and washed 5 times with water and once with brine. The resulting solution was passed through a silica pad, evacuated under reduced pressure and dispersed in pentane. Filtration of the suspension afforded pure **8** (0.380 g, 99%) as an orange powder.



HRMS ESI- [M⁻] m/z calculated = 914.1192; found 914.1190

NMR (¹H, CDCl₃, 400 MHz) δ (ppm) 8.77 (s, 4H), 2.38 (s, 6H), 2.18 (s, 6H), 1.69 (s, 18H); (¹³C, CDCl₃, 400MHz) δ (ppm) 161.47, 149.29, 148.37, 141.27, 135.74, 133.67, 131.72, 129.05, 123.74, 123.01, 116.84, 85.51, 28.04, 12.76, 11.98

Synthesis of 9: 8 (0.110 g, 120 μ mol) was introduced in a flame-dried sealable schlenk tube and exposed to high vacuum for 20 min. Potassium fluoride (0.070 g, 1.2 mmol, 10 eq) and



18-crown-6 (0.634 g, 2.4 mmol, 20 eq) were then added under argon atmosphere and further exposed to high vacuum for 10 min. Dry THF (15 mL) was then added under argon atmosphere, followed by ethane-1,2-dithiol (50 μL, 600 μmol, 5 eq). The resulting dark orange solution was stirred strongly under argon atmosphere at 85°C. Over the course of 1h, color gradually changed toward deep dark blue. After 1h30min, heating was turned off and the solution was left stirring in the now cooling oil bath for 15h. Eventually, the dark green solution was brought back to room temperature and dropped on water. The suspended solid was recovered by filtration and generously washed with water. It was then dissolved in dichloromethane and the layers were separated. The organic phase was washed once with brine and dried over magnesium sulfate. Solvents were evacuated and the solid was taken in AcoEt/cyclohexane mixture (50:50) and passed through a silica pad.

[NB: It is worth to notice that two fractions are observable at this point, undistinguishable in NMR and systematically of equivalent intensity and close R_f on thin layer chromatography. These are possibly due to conformation isomers, generated by the methyl groups of the pyrazole moiety, forbidding rotation and hence generating cis and trans conformers.]

Nevertheless, both fractions were combined and solvents were evacuated. The resulting solid was taken in ice-cold methanol and recovered by filtration. The dark solid was then washed with ice-cold methanol until the generated filtrate flowed slightly blue, affording pure **9** (0.090 g, 78%) as a dark purple-blue powder.

HRMS ESI– [M⁻] m/z calculated 958.1947; found 958.1927

NMR (¹H, CDCl₃, 400 MHz) δ (ppm) 8.97 (s, 4H), 3.37 (m, 8H), 2.39 (s, 6H), 2.19 (s, 6H), 1.69 (18H) (¹³C, CDCl₃, 400MHz) δ (ppm) 162.22, 149.48, 148.46, 141.20, 139.31, 133.90, 126.35, 122.01, 117.28, 85.53, 30.84, 28.06, 12.71, 11.96

Synthesis of 10: 9 (0.090 g, 93.8 μ mol) was dissolved in dichloromethane (20 mL) at room temperature and shielded from light. *Meta*-chloroperoxybenzoic acid (0.325 g, 1.88 mmol, 20 eq) was then added in one portion, under strong stirring. Color promptly changed from dark blue to deep redish pink. Eventually, the medium was filtered through a magnesium sulfate pad and solvents were evacuated. The dry solid was dissolved in the minimal amount of dichloromethane and purified by column chromatography (silica gel, liquid deposition (in DCM), cyclohexane/AcOEt (7:3), gradient elution 6:4 – 5:5 – 4:6 – 3:7). The fraction



containing the product were combined and evacuated under reduced pressure. The sticky solid was taken again in a 1:1 mixture of dichloromethane/trifluoroacetic acid (8 mL) and stirred at room temperature for 1h30min. Eventually, solvents were evacuated under reduced pressure. Trifluoroacetic

acid was again co-evaporated with dichloromethane (15 mL), twice. The resulting pink powder was dispersed in cyclohexane, recovered by vacuum filtration and washed with a 1:5 mixture of dichloromethane/cyclohexane, affording pure **10** (0.080 g, 96%) as a pink powder.

HRMS ESI– $[M-H^-]$ m/z calculated 886.0492; found 886.0487

NMR (¹H, *d*¹-TFA, 400 MHz) δ (ppm) 9.49 (s, 4H), 4.45 (d, J = 11.80 Hz, 4H), 4.27 (d, J = 11.80 Hz, 4H),

2.41 (s, 12H); (¹³C, *d*¹-TFA, 400MHz) δ (ppm) 145.37, 143.42, 134.36, 131.97, 130.02, 125.58, 124.49, 50.34, 7.92

Discussion: Chlorine substitution to sulfide

Several facts tend to indicate that the chlorine substitution (*i.e.* synthesis of **4** and synthesis of **8**) reaction goes by a radical, generated by an electron transfer from F^- to PDI:

- i) It has been established that fluoride anions are able to reduce even poorly-deficient unsubstituted PDI, through thermally activated electron transfer.^{4,5}
- ii) This feature has been used for sensing and for the chemical modifications of PDI such as the one considered here.^{6,7}
- iii) Several radical mechanisms have been proposed for this kind of substitution, with either halogenated or unsubstituted PDI.^{7–9} In the specific case of *bay*-substituted PDIs, Würthner *et al.* proposed a classical Radical-nucleophilic aromatic substitution mechanism (S_{RN}1), without the use of strong Lewis base such as F⁻.⁸ This mechanism and these conditions implies the formation of partially substituted to unsubstituted PDI *via* an H-abstraction step.

In the case of unsubstituted PDI, direct alkylthio-functionalization is possible with the use of F^- . In this situation, Fernández-Lázaro *et al.* propose a purely radical pathway.⁹ The aromaticity of the PDI core could be recovered by a loss of hydride, previously discussed for PDI.¹⁰

Unsubstituted products (*ergo* by loss of chlorine at *bay* positions) are not observed in our situation. This might be explained by the fact that F^- are able to reduce such dehalogenated PDI and bring them back in the $S_{RN}1$ cycle.

iv) Experimentally, prior to the addition of the thiol, heating of PDI-Cl 4 or boc-PDI-Cl 8 in presence of KF and 18-C-6 in THF results in the progressive change of color from orange to light blue, which can be associated with the formation of reduced PDI species. Additionally, at the end of the reaction, a deep dark green color was observed, that promptly disappeared upon vial opening and exposure to ambient air. This latter observation is compatible with the presence of reduced thionylated PDI products.

With these information in mind, we can propose the following mechanistic scheme (Scheme R1), summarizing our ideas.

For sake of clarity, this scheme does not underline that the H-abstraction pathway is susceptible to occur after any of the 4 chloride elimination steps and not only after the first one.



Scheme S1: Proposed mechanism for the thionylation reaction of chloro PDI.

Optical and electrochemical properties



Figure S1: Absorption (plain line) and emission (dotted line) spectra of PDI-Cl in THF (brown) and THF/HCl aq. 2M, 9:1 (orange). Excitation was performed at the maximum of absorption. Inset is a picture of similar solutions exposed to a 405nm laser beam (P < 5 mW)

Several examples report that excited PDI are able to undergo intramolecular photo-induced electron transfer (iPeT), effectively quenching their luminescence, if their structure include a relevant donor substituent.^{11–14} The possibility that dimethylpyrazole is involved this quenching process is supported by the fact that luminescence is observable in acidic media. Indeed, protonation of the pyrazole will increase its electron deficiency, and thus prevent a possible iPeT toward a PDI-centered orbital, depleted by excitation. We believe that boc protecting groups will act in a similar way.

We tried to verify the iPeT assumption *via* theoretical calculation. A simple and efficient way to do so is to perform single-point excitation from the optimized ground-state of PDI-Cl. Classical conditions for iPeT are met if i) the lowest energy bright transition involves two molecular orbitals (MO) centered on the PDI and ii) an occupied orbital, centered on the pyrazole, is higher in energy that the starting orbital involved in the transition. Such a situation is exemplified in the work of Staubitz *et al.*¹⁵

Unfortunately, in our situation, such conditions were close but not clearly met, regardless of the functional used for the computations (PBE1PBE, M062X or $\omega\beta$ 97XD). The only bright transition was always found to be HOMO-LUMO, with both MO located on the PDI core. The first orbital centered on the pyrazole was always the HOMO-1, with at least $\Delta E = -0.33$ eV lower energy than the HOMO. However, running the same computational study for a protonated version of PDI-Cl showed that the HOMO-1 is now much lower in energy than the HOMO and not centered on the pyrazole moiety anymore (see Figure S2).

If an iPeT seems not to be occurring in PDI-Cl, protonation clearly eliminates the probability of such a process in H⁺-PDI-Cl. Hence, given the proximity of the HOMO and HOMO-1 in PDI-Cl and the superficiality of this study, we cannot conclude with absolute certainty that iPeT is not occuring in PDI-Cl.



Figure S2: MO energy diagram for the neutral PDI-Cl and the doubly protonated H⁺-PDI-Cl

Other common deactivation pathways such as photo-induced energy transfer or twist induced charge transfer (TICT) seem unlikely to happen as the first should involve overlap between pyrazole absorption and PDI emission, and the second requires free rotation of the pyrazole, which is prevented by methyl groups.



Stability of the mono- and bis-reduced species

Figure S3. UV-Vis spectra showing the stability of the di and mono reduced species in acetonitrile; a) PDISO2 and b) PDISO2Et after addition of cobaltocene; c) PDISO2 and d) PDISO2Et after addition of 1 eq of triethylamine. Insets represent the variation of absorbance at specified wavelengths over time. All solutions have been prepared under ambient conditions.



Figure S4. UV-Vis spectra showing the stability of the di and mono reduced species in DMF; a) **PDISO2** and b) **PDISO2Et** after addition of cobaltocene; for c) **PDISO2** and d) **PDISO2Et** spontaneous reduction occurred over time in pure DMF. Insets represent the variation of absorbance at specified wavelengths over time. All solutions have been prepared under ambient conditions.

The UV-Vis spectra highlight very good robustness of the di-reduced species obtained upon addition of cobaltocene as reductant to acetonitrile or DMF solutions of the PDI ligands. Notably, the absorbance at 630 nm of PDI-SO2²⁻ decreased only by less than 4% in either ACN or DMF solvent over a 13 days period, reflecting its excellent stability in ambient conditions. The absorbance of PDI-SO2Et²⁻ in turn, showed a decrease of 14% under the same conditions.

Regarding the mono-reduced species, after addition of 1 eq of triethylamine, the radical anion of PDI-SO2 is gradually formed in acetonitrile over a period of 13 days along with the disappearance of the neutral species (FigS3c). Interestingly, under the same conditions, PDISO2Et spontaneously formed its radical anion species and then progressively evolved towards the di-reduced form (FigS3d). This observation is in line with the more anodically shifter reduction potential of PDI-SO2Et.

Remarquably, in DMF without any additive, the dianionic species PDISOEt²⁻ formed quantitatively after 3 days and then remained stable over the 13 days period (FigS4d).

Computational results



Figure S5: Spin density difference for a. PDI-Cl⁻⁻, b. PDI-SO₂⁻⁻ and c. PDI-SO₂eth⁻⁻. The gain in spin density is depicted in red and the loss in cyan. Atomic colors (A-color) are H-white, C-grey, N-blue, O-red and S-yellow. The isovalue used for the spind density is 0.0006.





in neutral state PDI⁰.



Table S2: Main values of the computed properties of every PDI, as depicted of the leftside of the table, in radical anion state PDI*-.



Table S3: Main values of the computed properties of every PDI, as depicted of theleft side of the table, in radical anion state PDI2-.

 $PDI-SO_2$ sulfone groups can rotate around the C_{core} —S bond. Hence, to extreme conformers are identifiable : i) one with each methyl groups pointing axially from the plane of the related naphtyl moiety, name $PDI-SO_2$ meth_exter and ii) one with each methyl group in the equatorial plane of each



Figure S7: Computed representation of a.) PDI-SO₂methexter and b.) PDI-SO₂oxexter

naphtyl moiety, named PDI-SO₂oxexter (see Figure S4). The computed free energy of each form indicates that only 1.57 kcal/mol separates these two forms, thus allowing both to exist stochastically.

¹H and ¹³C NMR Spectra



3_Pyrazol-NH2

















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



Atomic coordinates for the optimized structures

bPDI-Cl

С	0.000000	-0.000000	2.834306
С	0.000000	-0.000000	1.422856
С	-0.404398	1.165985	3.526121
С	-0.184234	1.227614	0.711505
С	-0.728564	2.296153	1.421683
С	-0.825655	2.270965	2.827603
Н	-1.214009	3.134008	3.358681
С	-0.426353	1.172236	5.010799
0	-0.786631	2.124387	5.676252
С	0.426353	-1.172236	5.010799
0	0.786631	-2.124387	5.676252
Ν	0.000000	-0.000000	5.618692
С	0.184234	1.227614	-0.711505
С	0.000000	-0.000000	-1.422856
С	0.728564	2.296153	-1.421683
С	0.000000	-0.000000	-2.834306
С	0.825655	2.270965	-2.827603
С	0.404398	1.165985	-3.526121
Н	1.214009	3.134008	-3.358681
С	0.404398	-1.165985	3.526121
С	0.825655	-2.270965	2.827603
Н	1.214009	-3.134008	3.358681
С	0.728564	-2.296153	1.421683
С	0.184234	-1.227614	0.711505
С	-0.184234	-1.227614	-0.711505
С	-0.728564	-2.296153	-1.421683
С	-0.404398	-1.165985	-3.526121
С	-0.825655	-2.270965	-2.827603
Н	-1.214009	-3.134008	-3.358681
С	0.426353	1.172236	-5.010799
С	-0.426353	-1.172236	-5.010799
Ν	0.000000	-0.000000	-5.618692
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0	0.786631	2.124387	-5.676252
Н	0.000000	0.000000	-6.636217
Н	-0.000000	0.000000	6.636217
Cl	1.430355	-3.671539	0.633374
Cl	-1.430355	-3.671539	-0.633374
Cl	1.430355	3.671539	-0.633374
Cl	-1.430355	3.671539	0.633374

bPDI-Cl•-

С	0.000000	-0.000000	2.837882
С	0.000000	-0.000000	1.412682
С	-0.356160	1.182010	3.527524
С	-0.167988	1.229650	0.702566
С	-0.687320	2.326214	1.433918
С	-0.765364	2.308605	2.816580
Н	-1.158641	3.164860	3.355199
С	-0.371994	1.193444	4.991232
0	-0.684267	2.160134	5.679958
С	0.371994	-1.193444	4.991232
0	0.684267	-2.160134	5.679958
Ν	0.000000	-0.000000	5.597159
С	0.167988	1.229650	-0.702566
С	0.000000	-0.000000	-1.412682
С	0.687320	2.326214	-1.433918
С	0.000000	-0.000000	-2.837882
С	0.765364	2.308605	-2.816580
С	0.356160	1.182010	-3.527524
Н	1.158641	3.164860	-3.355199
С	0.356160	-1.182010	3.527524
С	0.765364	-2.308605	2.816580
Н	1.158641	-3.164860	3.355199
С	0.687320	-2.326214	1.433918
С	0.167988	-1.229650	0.702566
С	-0.167988	-1.229650	-0.702566
С	-0.687320	-2.326214	-1.433918
С	-0.356160	-1.182010	-3.527524
С	-0.765364	-2.308605	-2.816580
Н	-1.158641	-3.164860	-3.355199
С	0.371994	1.193444	-4.991232
С	-0.371994	-1.193444	-4.991232
Ν	0.000000	-0.000000	-5.597159
0	-0.684267	-2.160134	-5.679958
0	0.684267	2.160134	-5.679958
Н	0.000000	0.000000	-6.613732
Н	-0.000000	0.000000	6.613732
Cl	1.450403	-3.671721	0.620808
Cl	-1.450403	-3.671721	-0.620808
Cl	1.450403	3.671721	-0.620808
Cl	-1.450403	3.671721	0.620808

bPDI-Cl²⁻

С	0.000000	-0.000000	2.843567
С	0.000000	-0.000000	1.405587
С	-0.307695	1.197166	3.530226
С	-0.153126	1.230250	0.694849
С	-0.648848	2.355791	1.443061
С	-0.713648	2.343223	2.805795
Н	-1.124191	3.188151	3.350348
С	-0.318419	1.212412	4.973039
0	-0.586075	2.191069	5.687056
С	0.318419	-1.212412	4.973039
0	0.586075	-2.191069	5.687056
Ν	0.000000	-0.000000	5.575810
С	0.153126	1.230250	-0.694849
С	0.000000	-0.000000	-1.405587
С	0.648848	2.355791	-1.443061
С	0.000000	-0.000000	-2.843567
С	0.713648	2.343223	-2.805795
С	0.307695	1.197166	-3.530226
Н	1.124191	3.188151	-3.350348
С	0.307695	-1.197166	3.530226
С	0.713648	-2.343223	2.805795
Н	1.124191	-3.188151	3.350348
С	0.648848	-2.355791	1.443061
С	0.153126	-1.230250	0.694849
С	-0.153126	-1.230250	-0.694849
С	-0.648848	-2.355791	-1.443061
С	-0.307695	-1.197166	-3.530226
С	-0.713648	-2.343223	-2.805795
Н	-1.124191	-3.188151	-3.350348
С	0.318419	1.212412	-4.973039
С	-0.318419	-1.212412	-4.973039
Ν	0.000000	-0.000000	-5.575810
0	-0.586075	-2.191069	-5.687056
0	0.586075	2.191069	-5.687056
Н	0.000000	0.000000	-6.591651
Н	-0.000000	0.000000	6.591651
Cl	1.475053	-3.665313	0.604929
Cl	-1.475053	-3.665313	-0.604929
Cl	1.475053	3.665313	-0.604929
Cl	-1.475053	3.665313	0.604929

bPDI-SO₂

С	-0.000000	-0.000000	2.830826
С	-0.000000	-0.000000	1.416476
С	-0.430057	1.153247	3.526798
С	-0.207256	1.227922	0.709083
С	-0.762572	2.287354	1.424447
С	-0.874564	2.248109	2.827957
Н	-1.268528	3.106754	3.364810
С	-0.454766	1.159404	5.013534
0	-0.844338	2.103226	5.671874
С	0.454766	-1.159404	5.013534
0	0.844338	-2.103226	5.671874
Ν	-0.000000	-0.000000	5.623209
С	0.207256	1.227922	-0.709083
С	0.000000	-0.000000	-1.416476
С	0.762572	2.287354	-1.424447
С	0.000000	-0.000000	-2.830826
С	0.874564	2.248109	-2.827957
С	0.430057	1.153247	-3.526798
Н	1.268528	3.106754	-3.364810
С	0.430057	-1.153247	3.526798
С	0.874564	-2.248109	2.827957
Н	1.268528	-3.106754	3.364810
С	0.762572	-2.287354	1.424447
С	0.207256	-1.227922	0.709083
С	-0.207256	-1.227922	-0.709083
С	-0.762572	-2.287354	-1.424447
С	-0.430057	-1.153247	-3.526798
С	-0.874564	-2.248109	-2.827957
Н	-1.268528	-3.106754	-3.364810
С	0.454766	1.159404	-5.013534
С	-0.454766	-1.159404	-5.013534
Ν	0.000000	-0.000000	-5.623209
0	-0.844338	-2.103226	-5.671874
0	0.844338	2.103226	-5.671874
С	-3.316006	3.119594	0.749853
Н	-3.400780	2.220577	0.138042
Н	-3.593392	2.927884	1.787061
Н	-3.920050	3.929250	0.333482
С	3.316006	3.119594	-0.749853
Н	3.400780	2.220577	-0.138042
Н	3.593392	2.927884	-1.787061
Н	3.920050	3.929250	-0.333482
С	-3.316006	-3.119594	-0.749853
Н	-3.400780	-2.220577	-0.138042
Н	-3.593392	-2.927884	-1.787061

Н	-3.920050	-3.929250	-0.333482
С	3.316006	-3.119594	0.749853
Н	3.593392	-2.927884	1.787061
Н	3.920050	-3.929250	0.333482
Н	3.400780	-2.220577	0.138042
Н	0.000000	0.000000	-6.640958
Н	-0.000000	0.000000	6.640958
S	-1.627025	3.700436	0.691407
S	1.627025	-3.700436	0.691407
S	1.627025	3.700436	-0.691407
S	-1.627025	-3.700436	-0.691407
0	1.269309	-3.857212	-0.719648
0	1.504207	-4.830893	1.609198
0	-1.504207	-4.830893	-1.609198
0	-1.269309	-3.857212	0.719648
0	-1.269309	3.857212	-0.719648
0	-1.504207	4.830893	1.609198
0	1.504207	4.830893	-1.609198
0	1.269309	3.857212	0.719648

bPDI-SO2 •-

С	0.000000	-0.000000	2.832228
С	0.000000	-0.000000	1.404456
С	-0.386907	1.168112	3.526780
С	-0.191353	1.231726	0.698787
С	-0.731892	2.318308	1.436068
С	-0.823379	2.281619	2.819747
Н	-1.228223	3.130959	3.362204
С	-0.406959	1.179373	4.995040
0	-0.752747	2.136874	5.674841
С	0.406959	-1.179373	4.995040
0	0.752747	-2.136874	5.674841
Ν	0.000000	-0.000000	5.603676
С	0.191353	1.231726	-0.698787
С	0.000000	-0.000000	-1.404456
С	0.731892	2.318308	-1.436068
С	0.000000	-0.000000	-2.832228
С	0.823379	2.281619	-2.819747
С	0.386907	1.168112	-3.526780
Н	1.228223	3.130959	-3.362204
С	0.386907	-1.168112	3.526780
С	0.823379	-2.281619	2.819747
Н	1.228223	-3.130959	3.362204
С	0.731892	-2.318308	1.436068
С	0.191353	-1.231726	0.698787

С	-0.191353	-1.231726	-0.698787
С	-0.731892	-2.318308	-1.436068
С	-0.386907	-1.168112	-3.526780
С	-0.823379	-2.281619	-2.819747
Н	-1.228223	-3.130959	-3.362204
С	0.406959	1.179373	-4.995040
С	-0.406959	-1.179373	-4.995040
Ν	0.000000	-0.000000	-5.603676
0	-0.752747	-2.136874	-5.674841
0	0.752747	2.136874	-5.674841
С	-3.311693	2.969708	0.649535
Н	-3.289711	2.077858	0.020861
Н	-3.628323	2.732794	1.665874
Н	-3.953376	3.736586	0.209685
С	3.311693	2.969708	-0.649535
Н	3.289711	2.077858	-0.020861
Н	3.628323	2.732794	-1.665874
Н	3.953376	3.736586	-0.209685
С	-3.311693	-2.969708	-0.649535
Н	-3.289711	-2.077858	-0.020861
Н	-3.628323	-2.732794	-1.665874
Н	-3.953376	-3.736586	-0.209685
С	3.311693	-2.969708	0.649535
Н	3.628323	-2.732794	1.665874
Н	3.953376	-3.736586	0.209685
Н	3.289711	-2.077858	0.020861
Н	0.000000	0.000000	-6.620498
Н	-0.000000	0.000000	6.620498
S	-1.666163	3.669037	0.703271
S	1.666163	-3.669037	0.703271
S	1.666163	3.669037	-0.703271
S	-1.666163	-3.669037	-0.703271
0	1.277388	-3.931872	-0.685477
0	1.684665	-4.778459	1.661582
0	-1.684665	-4.778459	-1.661582
0	-1.277388	-3.931872	0.685477
0	-1.277388	3.931872	-0.685477
0	-1.684665	4.778459	1.661582
0	1.684665	4.778459	-1.661582
0	1.277388	3.931872	0.685477

bPDI-SO₂²⁻

С	0.000000	-0.000000	2.836348
С	0.000000	-0.000000	1.396343
С	-0.342130	1.183579	3.528044

С	-0.177659	1.233522	0.690824
С	-0.711790	2.345356	1.444261
С	-0.784813	2.310292	2.811767
Н	-1.213288	3.144248	3.359292
С	-0.357551	1.198733	4.977796
0	-0.659830	2.167993	5.681096
С	0.357551	-1.198733	4.977796
0	0.659830	-2.167993	5.681096
Ν	0.000000	-0.000000	5.583815
С	0.177659	1.233522	-0.690824
С	0.000000	-0.000000	-1.396343
С	0.711790	2.345356	-1.444261
С	0.000000	-0.000000	-2.836348
С	0.784813	2.310292	-2.811767
С	0.342130	1.183579	-3.528044
Н	1.213288	3.144248	-3.359292
С	0.342130	-1.183579	3.528044
С	0.784813	-2.310292	2.811767
Н	1.213288	-3.144248	3.359292
С	0.711790	-2.345356	1.444261
С	0.177659	-1.233522	0.690824
С	-0.177659	-1.233522	-0.690824
С	-0.711790	-2.345356	-1.444261
С	-0.342130	-1.183579	-3.528044
С	-0.784813	-2.310292	-2.811767
Н	-1.213288	-3.144248	-3.359292
С	0.357551	1.198733	-4.977796
С	-0.357551	-1.198733	-4.977796
Ν	0.000000	-0.000000	-5.583815
0	-0.659830	-2.167993	-5.681096
0	0.659830	2.167993	-5.681096
С	-3.291919	2.764190	0.503839
Н	-3.134132	1.899113	-0.143676
Н	-3.652606	2.460952	1.487357
Н	-3.975271	3.476105	0.035211
С	3.291919	2.764190	-0.503839
Н	3.134132	1.899113	0.143676
Н	3.652606	2.460952	-1.487357
Н	3.975271	3.476105	-0.035211
С	-3.291919	-2.764190	-0.503839
Н	-3.134132	-1.899113	0.143676
Н	-3.652606	-2.460952	-1.487357
Н	-3.975271	-3.476105	-0.035211
С	3.291919	-2.764190	0.503839
Н	3.652606	-2.460952	1.487357
Н	3.975271	-3.476105	0.035211

Н	3.134132	-1.899113	-0.143676
Н	-0.000000	0.000000	-6.599906
Н	-0.000000	0.000000	6.599906
S	-1.726751	3.611640	0.701843
S	1.726751	-3.611640	0.701843
S	1.726751	3.611640	-0.701843
S	-1.726751	-3.611640	-0.701843
0	1.299493	-3.994873	-0.648721
0	1.924098	-4.679716	1.694208
0	-1.924098	-4.679716	-1.694208
0	-1.299493	-3.994873	0.648721
0	-1.299493	3.994873	-0.648721
0	-1.924098	4.679716	1.694208
0	1.924098	4.679716	-1.694208
0	1.299493	3.994873	0.648721

bPDI-SO₂eth

0	-2.674087	-1.563298	-4.044430
S	1.605859	-0.635654	3.676075
0	-1.924296	0.744683	-3.309248
С	0.453836	-0.604782	5.060296
S	-1.605862	-0.635647	-3.676074
С	0.768024	-1.416340	2.279730
Н	1.325101	-3.354393	3.081902
С	0.884497	-2.820179	2.245418
С	-0.453836	0.604782	5.060296
0	0.840030	-5.665780	2.105518
0	-0.840030	5.665780	2.105518
С	0.205218	-0.707714	1.224107
С	0.428656	-3.520716	1.155523
С	0.454753	-5.007522	1.160193
С	-0.454753	5.007522	1.160193
С	-0.205218	0.707714	1.224107
С	-0.428656	3.520716	1.155523
С	-0.884497	2.820179	2.245418
С	-0.000002	-2.826758	0.000001
С	-0.768030	-1.416341	-2.279731
С	-0.000001	-1.414607	-0.000001
Ν	-0.000002	5.616028	0.000001
С	0.000001	1.414607	-0.000001
С	-0.768024	1.416340	2.279730
С	0.000002	2.826758	0.000001
С	-0.884494	-2.820181	-2.245418
С	-0.428656	-3.520718	-1.155520
Ν	0.000002	-5.616028	0.000001

С	-0.205220	-0.707714	-1.224109
Н	-1.107870	-0.581698	-5.937867
С	-0.454747	-5.007523	-1.160192
С	0.454747	5.007523	-1.160192
С	0.428656	3.520718	-1.155520
С	0.205220	0.707714	-1.224109
Н	-1.325088	-3.354402	-3.081902
Н	-1.325101	3.354393	3.081902
0	-0.840020	-5.665782	-2.105519
Н	-0.096893	1.549252	-5.050097
0	0.840020	5.665782	-2.105519
С	-0.453840	-0.604779	-5.060298
С	0.884494	2.820181	-2.245418
S	-1.605859	0.635654	3.676075
С	0.768030	1.416341	-2.279731
С	0.453840	0.604779	-5.060298
Н	1.325088	3.354402	-3.081902
S	1.605862	0.635647	-3.676074
Н	0.096893	-1.549252	-5.050097
Н	1.107870	0.581698	-5.937867
0	1.924296	-0.744683	-3.309248
0	2.674087	1.563298	-4.044430
Н	0.000003	-6.633806	0.000001
Н	-0.000003	6.633806	0.000001
Н	1.107861	-0.581709	5.937869
Н	-0.096904	-1.549251	5.050089
Н	0.096904	1.549251	5.050089
Н	-1.107861	0.581709	5.937869
0	-1.924304	-0.744676	3.309258
0	-2.674076	1.563319	4.044418
0	2.674076	-1.563319	4.044418
0	1.924304	0.744676	3.309258

bPDI-SO₂eth •-

0	-2.630193	1.632493	4.093701
S	1.588910	0.680804	-3.691991
0	-1.966068	-0.690833	3.337840
С	0.445234	0.610761	-5.083595
S	-1.588910	0.680804	3.691991
С	0.726491	1.432577	-2.315309
Н	1.246575	3.365080	-3.116136
С	0.814213	2.819180	-2.283064
С	-0.445234	-0.610761	-5.083595
0	0.726746	5.671140	-2.145886
0	-0.726746	-5.671140	-2.145886
С	0.187499	0.697413	-1.229769
С	0.375955	3.523808	-1.171490
С	0.395232	4.993534	-1.182932
С	-0.395232	-4.993534	-1.182932
С	-0.187499	-0.697413	-1.229769
С	-0.375955	-3.523808	-1.171490
С	-0.814213	-2.819180	-2.283064
С	0.000000	2.828090	-0.000000
С	-0.726491	1.432577	2.315309
С	0.000000	1.402550	-0.000000
Ν	-0.000001	-5.602334	0.000000
С	-0.000000	-1.402550	-0.000000
С	-0.726491	-1.432577	-2.315309
С	-0.000000	-2.828090	-0.000000
С	-0.814213	2.819180	2.283064
С	-0.375955	3.523808	1.171489
Ν	0.000001	5.602334	0.000000
С	-0.187499	0.697413	1.229769
Н	-1.101094	0.594766	5.959465
С	-0.395232	4.993534	1.182932
С	0.395232	-4.993534	1.182932
С	0.375955	-3.523808	1.171489
С	0.187499	-0.697413	1.229769
Н	-1.246575	3.365080	3.116136
Н	-1.246575	-3.365080	-3.116136
0	-0.726743	5.671140	2.145886
Н	-0.122713	-1.544874	5.077547
0	0.726743	-5.671140	2.145886
С	-0.445234	0.610761	5.083595
С	0.814213	-2.819180	2.283064
S	-1.588910	-0.680804	-3.691991
С	0.726491	-1.432577	2.315309
С	0.445234	-0.610761	5.083595
Н	1.246575	-3.365080	3.116136

S	1.588910	-0.680804	3.691991
Н	0.122713	1.544874	5.077547
Н	1.101094	-0.594766	5.959465
0	1.966068	0.690833	3.337840
0	2.630193	-1.632493	4.093701
Н	0.000001	6.619190	0.000000
Н	-0.000001	-6.619190	0.000000
Н	1.101094	0.594766	-5.959465
Н	-0.122713	1.544874	-5.077547
Н	0.122713	-1.544874	-5.077547
Н	-1.101094	-0.594766	-5.959465
0	-1.966068	0.690833	-3.337840
0	-2.630193	-1.632492	-4.093701
0	2.630193	1.632492	-4.093701
0	1.966068	-0.690833	-3.337840

bPDI-SO₂eth²⁻

0	2.587480	1.698372	-4.143365
S	-1.573753	0.724319	3.708688
0	2.006806	-0.636510	-3.365870
С	-0.437372	0.616148	5.105959
S	1.573758	0.724325	-3.708690
С	-0.689787	1.447563	2.348725
Н	-1.185409	3.375283	3.142310
С	-0.753978	2.819060	2.315513
С	0.437372	-0.616148	5.105959
0	-0.625573	5.679820	2.177693
0	0.625573	-5.679820	2.177693
С	-0.171965	0.688995	1.234105
С	-0.325363	3.528831	1.185689
С	-0.340480	4.980799	1.201839
С	0.340480	-4.980799	1.201839
С	0.171965	-0.688995	1.234105
С	0.325363	-3.528831	1.185689
С	0.753978	-2.819060	2.315513
С	0.000006	2.832102	0.000001
С	0.689790	1.447565	-2.348726
С	0.000011	1.394034	0.000004
Ν	-0.000015	-5.588528	0.000006
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С	-0.000006	-2.832102	0.000001
С	0.753978	2.819059	-2.315516

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Ν	0.000015	5.588528	0.000006
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С	-0.340484	-4.980796	-1.201835
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С	-0.437361	-0.616155	-5.105954
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Н	-0.145875	-1.540781	5.103136
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0	2.587475	-1.698373	4.143354
0	-2.587475	1.698373	4.143354
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