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Electronic Supplementary Information for

Transition metal complexes of axially chiral tetrathioether baysubstituted perylene bisimide dye

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1. Experimental Details and Synthesis

1.1 Materials and methods:

Potassium carbonate (\geq 99%), *n*-butylthiol, tetrabutylammonium tetrafluoroborate [(*n*-Bu)₄NBF₄] bis(acetonitrile)dichloropalladium [PdCl₂(MeCN)₂] and *N*-methyl-2-pyrrolidone (NMP, 99.5%) were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. NMP was fractionally distilled prior to use and potassium carbonate was dried in vacuo at 100 °C for 24 h. The starting material *N*, *N'*-dicyclohexyl-1,6,7,12-tetrachloroperylene-3,4:9,10- tetracarboxylic acid bisimide (PBI **1**) was prepared according to the literature.^{S1,S2} Flash column chromatography was performed using silica gel (Si60, mesh size 40-63 µm) from Merck. NMR spectra were recorded with a Bruker Avance 400 MHz instruments. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. ¹H coupling constants *J* are given in Hertz (Hz). MALDI-TOF mass spectra were recorded on an Autoflex II from Bruker Daltonics spectrometer.

All the solvents used for the spectroscopic measurements are of spectroscopic grade (Uvasol®) and are used without further purification. The UV-Vis spectra were recorded on a Perkin Elmer PE 950 spectrometer equipped with a PTP-1 peltier element, and corrected against the reference solution (solvents or solvents with the same amount of TBAH). The fluorescence spectra were recorded with a PTI QM-4/2003 instrument. All fluorescence measurements were performed under ambient conditions and corrected against photomultiplier and lamp intensity. The fluorescence quantum yields were determined as the average value for three different excitation wavelengths using N,N^{2} -di(2,6-di-isopropylphenyl)-perylene-3,4:9,10-tetracarboxylic acid bisimide as reference ($\Phi_{fl} = 1.00$ in dichloromethane^{S3}) by applying high dilution conditions (A < 0.05). Circular dichroism (CD) measurements were carried out on a JASCO J-810 spectrometer equipped with a CDF 426-S temperature control unit.

Recycling semipreparative HPLC was carried out on a system with a photodiode array detector and a Reprosil 100 Chiral-NR chiral column from Trentec (Gerlingen, Germany, size $\emptyset = 20$ mm). The experiments were performed with HPLC grade dichloromethane and a flow rate of 3.5 mL/min. For the kinetic measurements by time-dependent CD spectroscopy, the atropo-enantiomers of **2** were separated by semipreparative HPLC and to gain the highest possible *ee* value only the outer edge of the respective enantiomer peaks were taken. The obtained fractions were dried by nitrogen flow and afterwards stored at -20 °C. At the beginning of the measurement the enantiomer was dissolved in degassed 1,1,2,2,-tetrachloroethane (1,1,2,2-tetrachloroethane used for the CD measurements was fractionally distilled under vacuum prior to use). The Peltier element was calibrated to the starting temperature and the starting time was defined when the temperature was constant. For data evaluation, the Eyring (equation 4 and 5) and Arrhenius equation (equation 3) were applied as outlined in section 5 of the ESI. The errors for the rate constant k, activation energy E_A , enthalpy ΔH^{\ddagger} and entropy of activation ΔS^{\ddagger} are the standard deviation obtained by linear regression analysis. The errors for ΔG^{\ddagger} and $t_{1/2}$ were calculated by main error estimation.

1.2 Synthesis and Characterization:

Synthesis of PBI 2: A portion of 3.0 mL (28.0 mmol) n-butylthiol, 2.30 g (3.33 mmol) PBI 1, 2.0 g (6.1 mmol) (n-Bu)₄NBF₄ and 2.80 g (20.4 mmol) K₂CO₃ were suspended in 50 mL dry DMF and stirred under argon at 120 °C for 72 hours. After being cooled to room temperature, the reaction mixture was dropped into 250 mL 1 N HCl under stirring. The solid was separated by filtration, and then washed successively with water (3×30 mL) and methanol (3×30 mL) methanol (3×30 mL) and methanol (3×30 mL) anol (3×30 mL) and methanol (3×30 mL) and methan 30 mL). The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as an eluent. After removal of the solvent with rotary evaporator, 1.35 g (yield: 45%) of PBI 2 were obtained as a purple solid. m. p. > 300 °C; ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ = 8.68 (s, 4H), 5.07-5.01 (m, 2H), 2.98-2.94 (m, 8H), 2.52-2.43 (m, 4H), 1.85-1.82 (d, J = 12.0 Hz, 4H), 1.72-1.64 (m, 6H), 1.39-1.36 (m, 6H), 1.32-1.21 (m, 8H), 1.14-1.09 (m, 8H), 0.62-0.58 (m, 12H); ¹³C NMR (150 MHz, CD₂Cl₂, ppm): δ = 164.1, 139.6, 132.1, 131.7, 129.4, 123.2, 122.2, 117.0, 36.9, 31.2, 25.9. 22.1. 29.5. 29.4. 26.9. 13.6; MALDI-TOF (CHCl₃ solution of PBI 2. matrix: trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile, mode: negative): m/z calcd for C₅₂H₆₂N₂O₄S₄, 906.36 [M]⁻, found, 906.30. UV-Vis (CH₂Cl₂): λ_{max} (ϵ/L mol⁻¹ cm⁻¹) = 565 (21020), 337 (15820), 293 (27900) nm.

Synthesis of PBI $[2 \cdot Ag_2]$ and $[2 \cdot Pd_2]$ complex: To a solution of PBI 2 (45.0 mg, 0.05 mmol) in CH₂Cl₂/MeOH (90:10, 4 mL), two equivalents of AgOTf (26.0 mg, 0.10 mmol) or PdCl₂(MeCN)₂ (26.0 mg, 0.10 mmol), resp., was added and the solution was stirred for 1 h at room temperature. The respective solution was concentrated and the product was precipitated by addition of 3 mL MeOH and isolated quantitatively by centrifugation.

[2·Ag₂]: ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ = 9.06 (s, 4H), 5.10-5.04 (m, 2H), 3.09-3.07 (m, 4H), 2.57-2.54 (m, 4H), 1.93-1.90 (d, *J* = 12.0 Hz, 4H), 1.79-1.73 (m, 6H), 1.50-1.43 (m, 6H), 1.21-0.98 (m, 16H), 0.54-0.50 (m, 12H); ¹³C NMR (150 MHz, CD₂Cl₂-CD₃CN, ppm): δ = 166.7, 139.3, 137.2, 135.3, 132.2, 129.1, 128.2, 127.0, 125.9, 122.7, 121.5, 119.5, 43.2, 34.2, 32.8, 30.2, 29.1, 25.0, 16.7. MALDI-TOF (CHCl₃ solution of [2·Ag₂], matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, mode: positive): *m*/*z* calcd. for C₅₄H₆₂Ag₂F₆N₂O₁₀S₆, 1272.12 [M-OTf]⁺ and 1013.26 [M-Ag(OTf)₂]⁺, found, 1272.12 and 1013.29. UV-Vis (CH₂Cl₂): λ_{max} (ε/L mol⁻¹ cm⁻¹) = 535 (18600), 334 (18300), 293 (27100) nm.

 $[2 \cdot Pd_2]: {}^{1}H NMR (400 MHz, CD_2Cl_2, ppm): \delta = 8.84 (s, 4H), 5.01-4.93 (m, 2H), 3.36-3.36 (m, 4H), 3.13-3.06 (m, 4H), 2.53-2.40 (m, 4H), 1.89-1.86 (d,$ *J*= 12.0 Hz, 4H), 1.75-1.68 (m, 6H), 1.33-1.25 (m, 6H), 1.18-1.06 (m, 16H), 1.49-1.86 (m, 16H), 1.49-1.8

0.59-0.56 (m, 12H); ¹³C NMR (150 MHz, CD₂Cl₂, ppm): $\delta = 161.7$, 135.0, 133.1, 132.4, 130.8, 128.2, 125.4, 117.0, 40.7, 31.0, 29.4, 29.3, 29.2, 26.8, 25.7, 21.6, 13.3. MALDI-TOF (CHCl₃ solution of [**2**·Pd₂], matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, mode: negative): m/z calcd for C₅₂H₆₂Cl₄N₂O₄Pd₂S₄, 1262.04 [M]⁻, found, 1261.58. UV-Vis (CH₂Cl₂): λ_{max} (ϵ/L mol⁻¹ cm⁻¹) = 620 (12600), 438 (14700) nm.

2. X-ray Diffraction Analysis

2.1 Methods and crystal data

The crystal data of $[2 \cdot Pd_2]$ were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo_{Ka} radiation. The structure was solved using direct methods, refined with the Shelx software package^{S4} and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions. The crystal was split with domains rotated by 6° around real axis [$-0.186 \quad 1.000 - 0.361$]. The minor domain had less than 3% of occupancy. For that reason de-twinned data (TwinAbs, HKLF 4 format) were used during refinement. Two ligands (SBu and cyclohexyl) in this structure were rotationally disordered. The displacement parameters (ADP) of atoms in these ligands were restrained using DELU keyword ('rigid bond' restraint for all bonds in the connectivity list). Additionally these ADPs were restrained to the same value with similarity restraint SIMU (Cy) or EADP constraint (SBu) and their tensors were refined isotropically with the ISOR keyword. The geometry of the disordered cyclohexyl group (minor component) was constrained on idealized geometry using AFIX 176.

Crystal data for [2·Pd₂]: C₅₈H₇₄Cl₁₆N₂O₄Pd₂S₄, $M_r = 1771.43$, red block, $0.22 \times 0.21 \times 0.07 \text{ mm}^3$, triclinic space group *P*-1, *a* = 12.7870(9) Å, *b* = 13.7386(10) Å, *c* = 21.6400(15) Å, *α* = 103.264(3)°, *β* = 94.378(3)°, *γ* = 100.247(3)°, *V* = 3613.8(4) Å³, *Z* = 2, $\rho_{calcd} = 1.628 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 1.250 \text{ mm}^{-1}$, *F*(000) = 1792, *T* = 103(2) K, *R_I* = 0.0347, $wR^2 = 0.0877$, 14122 independent reflections [20≤52.04°] and 831 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-946435. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

3. NMR and MALDI-TOF mass spectra



Figure S1: ¹H NMR spectra of PBI **2**, [**2**•Ag₂] and [**2**•Pd₂] in CD₂Cl₂ (400 Hz, 300 K).



Figure S2: MALDI-TOF mass spectrum of PBI **2** (from CHCl₃ solution of PBI **2**, matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, mode: negative), where the m/z at 906.3 is assigned to molecular ion peak of the $[M]^-$.



Figure S3: UV-Vis absorption (black line) and normalized emission (grey line) spectra of PBI 2 in dichloromethane at room temperature.



Figure S4: MALDI-TOF mass spectrum of $[2 \cdot Ag_2]$ (from CHCl₃ solution of $[2 \cdot Ag_2]$, matrix: *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile, mode: positive), where the*m/z* $at 1272.1 is assigned to ion peak of the <math>[M-OTf]^+$ and that at 1013.3 is assigned to the ion peak of $[M-Ag(OTf)_2]^+$.



Figure S5: MALDI-TOF mass spectrum of $[2 \cdot Pd_2]$ (from CHCl₃ solution of $[2 \cdot Pd_2]$, matrix: *trans*-2-[3-(4-*tert*-butylphenyl)- 2-methyl-2-propenylidene]malononitrile, mode: negative), where the m/z at 1261.6 is assigned to molecular ion peak of the $[M]^-$.

4. Separation and CD spectra of the atropo-enantiomers



Figure S6: Recycling HPLC chromatogram of the atropo-enantiomer separation of PBI **2** on Trentec Reprosil 100 chiral-NR column at ambient conditions using dichloromethane as eluent (flow rate: 3.5 mL/min).



Figure S7: Normalized circular dichroism spectra of both atropo-enantiomers of **2** in dichloromethane at 20 °C; first eluted fraction (black solid line), second eluted fraction (red dashed line). Accordingly to exciton chirality method^{S5} and our previously accomplished stereochemical assignment of enantiomeric pure macrocyclic PBI systems, ^{S6} the first eluted fraction can be tentatively assigned to the *P*-enantiomer and the second eluted fraction to the *M*-enantiomer.

5. Racemization kinetic experiments



Figure S8: Changes in the CD spectra of the *P*-2 enantiomer (the first eluted fraction) over 4 hours at 100 °C in degassed 1,1,2,2-tetrachloroethane.

The rate law of racemization process between P- and M-enantiomers is given by

$$v = -\frac{d(A)}{A_0} = kdt \tag{1}$$

where A is the concentration of the enantiomer which is present in excess and A_0 the respective initial

concentration.

The integrated form of the rate law is given by

$$\ln \frac{A}{A_0} = -kt \implies A = A_0 e^{-kt}$$
⁽²⁾

Owing to a linear relationship between CD amplitude and the concentration of initial enantiomer, the latter can be directly replaced by the experimentally determined CD intensity. According to equation (2), the rate constant at a certain temperature is determined from the exponential decay of the CD signal with respect to time as shown in Fig. S9 and can be used to calculate the half-life according to $t_{1/2} = \ln 2/k$. The half-lifes and rate constants of **2** at different temperatures are given in Table S1.



Figure S9: Exponential decay of the CD intensity of *P*-2 enantiomer (the first eluted fraction) at 368 K in degassed 1,1,2,2-tetrachloroethane. The detection wavelength was 470 nm.

The temperature dependence of the rate constant can be used to determine the activation energy of a process according to the Arrhenius equation (3) and the thermodynamic parameters of the transition state of a reaction expressed in the Eyring equation (4) and (5).

Arrhenius
$$k = Ae^{-\frac{E_A}{RT}} \Longrightarrow lnk = -\frac{E_A}{R}\frac{1}{T} + lnA$$
 (3)

$$\Delta G^{\dagger} = \Delta H^{\dagger} - T \Delta S^{\dagger} = -RT ln \frac{kh}{\kappa k_B T}$$
⁽⁴⁾

$$ln\frac{k}{T} = -\left(\frac{\Delta H^{\dagger}}{R}\right)\frac{1}{T} + \frac{\Delta S^{\dagger}}{R} + ln\frac{\kappa k_{B}}{h}$$
(5)

Eyring

Analysis of the racemization of
$$2$$
 with the Arrhenius and Eyring equations is shown in Fig. S10. The parameter κ was taken as 0.5 since the probability of the transition state to transform into one or the other stereoisomer is equal.



Figure S10: Temperature dependence of *k* for *P*-2 enantiomer (the first eluted fraction) according to the Arrhenius plot (left) and Eyring plot (right). Insets show the respective linear regression analysis.

Table S1: Kinetic data for the racemization process of PBI *P*-2 enantiomer (the first eluted fraction) in degassed 1,1,2,2-tetrachloroethane at different temperatures.

Τ/Κ	$k / 10^{-5} \mathrm{s}^{-1}$	$t_{1/2}^{a} / \min$	$\Delta G^{\ddagger} / \mathrm{kJ} \mathrm{mol}^{-1}$
363	2.84 ± 0.04	407 ± 6	119.1 ± 0.1
368	4.85 ± 0.03	238 ± 2	119.1 ± 0.1
370.5	6.81 ± 0.05	170 ± 1	118.9 ± 0.1
373	8.99 ± 0.04	129 ± 1	118.8 ± 0.1

^a Calculated according to $t_{1/2} = \ln 2/k$

6. UV-Vis and CD titration studies of PBI 2 with PdCl₂(MeCN)₂



Figure S11: UV-Vis spectroscopic titration of *P*-2 enantiomer (the first eluted fraction) with PdCl₂(MeCN)₂ in 0.2 eq. steps under ambient conditions in CH₂Cl₂/MeOH 9:1 and a waiting time of 10 min after each addition.



Figure S11: CD spectroscopic titration of P-2 enantiomer (the first eluted fraction) with PdCl₂(MeCN)₂ in 0.2 eq. steps under ambient conditions in CH₂Cl₂/MeOH 9:1 and a waiting time of 10 min after each addition. The inset shows the change of the CD intensity at 430 nm vs. addition of certain Pd equivalents.

7. References

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