Supporting information

1. General Methods and Procedures

The reaction was carried out in dry EtOH under an argon atmosphere and at room temperature. NMR spectrum was recorded with a Bruker Avance 300 spectrometer and all chemical shifts are reported relative to the solvent signal [CDCl₃: 7.26 ppm (¹H)]. The assignments of the NMR signals were carried out under using 2D-NMR experiments ¹H-¹H-COSY. IR spectra were recorded with a Thermo Nicolet NEXUS FTIR instrument. Elemental analyses (C,H,N,S) were performed with an Elementar Vario EL elemental analyzer. The EI spectra were recorded using Thermo Quest SSQ 710 (70eV). Melting point (m.p.) is measured with a capillary.

2. Synthesis

The commercial available 9,10-bis(chloromethyl)anthracene (5 g, 18.17 mmol) was added to a solution of disodium-1,2-dicyanoethene-1,2-dithiolate ¹ (3.38 g, 18.17 mmol) in ethanol (1.5 L). The resulting suspension was stirred for 24 h. After that the solvent was removed and the residue was dissolved in chloroform (0.9 L). The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness to yield a orange solid. This residue was purified by column chromatography on silica gel using CHCl₃ as an eluent to afford **1** as orange solid.

[6.6](9,10)anthracenophane **1**



Yield: 2.19 g (35 %); $R_f = 0.27$ CHCl₃; m.p.: 274 °C (decomp.); ¹H-NMR (300 MHz, CDCl₃): $\delta = 7.85$ (dd, 8H, ³ $J_{H,H} = 3.0$ Hz, 1-H), 7.58 (dd, ³ $J_{H,H} = 3.0$ Hz, 8H, 2-H), 4.94 ppm (s, 8H, 11-H); IR (KBr): $\tilde{v} = 3049$ (m), 2226 (m, (C=N)), 2202 (m, (C=N)), 1494 (m; (C=C)), 1430 (s), 1219 (s), 1164 (m), 768 (s), 703 cm⁻¹ (m); UV-VIS (thf): λ_{max} (ε) = 393 (17800), 374 nm (21300); fluorescence (thf): $\lambda_{max} = 597$, 450, 426, 406 nm; EI-MS: m/z (%): 688 (5) [M⁺]; 548

¹ G. Bähr and G. Schleitzer, *Chem. Ber.*, 1955, **88**, 1777.

(8) $[M-C_4N_2S_2]^+$, 484 (25) $[M-C_{16}H_{12}]^+$, 204 (100) $[M-C_{24}H_{12}N_4S_4]^+$; elemental analysis (%) calcd. for $C_{40}H_{24}N_4S_4$ 688.90): C 69.74 H 3.51 N 8.13 S 18.62; found: C 69.81 H 3.32 N 8.29 S 18.22

3. UV/Vis absorption measurements



Fig. 1 UV/Vis absorption spectra of 1-3 in THF; $c(1-3) = 5 \times 10^{-5}$ M.



Fig. 2 UV/Vis absorption spectra of 1 ($c(1) = 5 \times 10^{-5}$ M) in the presence of 0 (—), 0.2 (—), 0.4 (—), 0.6 (—), 0.8 (—), 1 (—), 1.2 (—), 1.4 (—), 1.6 (—), 1.8 (—), 2 (—) and 3 equiv. (—) [PdCl₂(C₆H₅CN)₂] in THF.



Fig. 3 Job plot of a 1:2-complex of $\mathbf{1}$ with PdCl₂.

UV/Vis spectra were recorded on a Analytik Jena Specord S 100 spectrophotometer using sealed quartz cuvettes. Titration of the ligand **1** ($c = 5 \cdot 10^{-5} \text{ mol} \cdot 1^{-1}$) was carried out by addition of microliter amounts of standard solutions of [PdCl₂(C₆H₅CN)₂] ($c = 5 \cdot 10^{-4} \text{ mol} \cdot 1^{-1}$) in THF. All solutions are degassed and between every step a period of 10 minutes was waited. All the spectra are concentration corrected.

Usually, complexation of a cation induces conformational reorientations of the cyclophane structure, which changes the degree of overlap between the anthracenic chromophores, and this directly affects the UV-Vis absorption spectrum.² [2.2]Anthracenophanes show the greater the overlap of the two chromophores in the sandwich conformation, the lower the integrated absorption intensity.³ However, Fig. S2 displays the absorption spectra of **1** taken in the course of titration with $[PdCl_2(C_6H_5CN)_2]$ in THF and the resulting titration curve at 404 nm. After addition of two equivalents of $PdCl_2$ to **1**, the ICT band is suppressed. Again, this is also supported by theoretical calculations for the $[(PdCl_2)_2(1)]$ -complex. The inset of Fig. S2 gives a hint at the complex's stoichiometry by a molar ratio of **1** : $PdCl_2$ of 1 : 2. Further, the resulting UV/Vis absorption spectrum of the $[(PdCl_2)_2(1)]$ -complex in solution displays a more pronounced and intense p-band compared to the free ligand **1** (see Fig. S1). This correlates with the theoretical calculations for $PdCl_2$ -complexes where the overlap of the anthracenic chromophores changes during $PdCl_2$ complexation (see Fig. S7), and thus increases the absorption intensity as discussed above. The stability constants of $PdCl_2$ -complexes were determined by using this spectrophotometric titration.

The formation of 1:1 and 1:2 complexes between the ligand [6.6](9,10] anthracenophane **1** ($[(C_6H_5CN)_2]$, [L]) and palladiumdichloride ($[PdCl_2]$, [M]) can be described by following reactions:

² C. Pascard, C. Riche, M. Cesario, F. Kotzyba-Hibert and J.-M Lehn, J. Chem. Soc., Chem. Commun., 1982, 557; H. Bouas-Laurent, A. Castellan, M. Daney, J.-P. Desvergne, G. Guinand, P. Marsau and M.-H. Riffaud, J. Am. Chem. Soc., 1986, **108**, 315; F. Fages, J.-P. Desvergne, K. Kampke, H. Bouas-Laurent, J.-M. Lehn, M. Meyer and A.-M. Albrecht-Gary, J. Am. Chem. Soc., 1993, **115**, 3658; D. Marquis, J.-P. Desvergne and H. Bouas-Laurent, J. Org. Chem., 1995, **60**, 7984, G. Nishimura, H. Maehara, Y. Shiraishi and T. Hirai, Chem. Eur. J., 2008, **14**, 259.

³ J. Ferguson, *Chem. Rev.*, 1986, **86**, 957.

$$[L] + [M] \stackrel{\kappa_{1}}{\longleftrightarrow} [LM]$$
$$[LM] + [M] \stackrel{\kappa_{2}}{\longleftrightarrow} [LM_{2}]$$
or:
$$[L] + 2[M] \stackrel{\beta = \kappa_{1} \cdot \kappa_{2}}{\longleftrightarrow} [LM_{2}]$$

The stability constants K₁ and K₂ are given by:

$$K_1 = \frac{[LM]}{[L] \cdot [M]}$$
 and $K_2 = \frac{[LM_2]}{[LM] \cdot [M]}$

The experimentally measured absorption A_i at a fixed wavelength (406 nm; palladiumdichloride [M] has no absorption at this wavelength) by a constant optical path length d can be described using the Lambert Beer equation:

$$A = d * \left(\epsilon_{L} [L] + \epsilon_{LM} [LM] + \epsilon_{LM_{2}} [LM_{2}] \right)$$

with the molar absorptivity of the ligand ε_L , and of the complexes ε_{LM} and ε_{LM_2} .

The calculation of the unknown extinction coefficients ϵ_{LM} and ϵ_{LM_2} and of the stability constants K_1 and K_2 was done by non-linear regression analysis. The calculated values are: log $K_1=7.36 \pm 0.43$, log $K_2=7.74 \pm 0.43$ and log $\beta=15.1 \pm 0.9$.

The experimental values of the UV/Vis absorption A_i (406 nm) at different equivalents of c_M to c_L and the calculated values of A are shown in Fig. 4.



Fig. 4 Experimental values of the UV/Vis absorption A_i and the calculated values of A at different equivalents of c_M to c_L in THF.

4. Fluorescence measurements

Fluorescene spectra were carried out with Fluoromax 3 HORIBA spectrometer using sealed quartz cuvettes. All solutions were degassed. The fluorescence quantum yields of 1 and 2

were measured using a solution of 9,10-diphenylanthracene ($\Phi_f=1$) in THF and CH₃CN as a standard. The exact determination of the very low Φ_f of **1** ($\Phi_f < 10^{-3}$) in solution was difficult because of the very low fluorescence intensity of **1** in the range of 450-700 nm and the complete disappearance of the anthracene part.



Fig. 5 Fluorescence emission spectra of 1 ($c(1) = 5 \times 10^{-6}$ M, $\lambda_{ex} = 350$ nm).

The conditions for the fluorescene titration were similar to the UV/Vis-titration. The excitation of **1** takes place at the isosbestic point (taken from UV/Vis-titration) **1**: 356 nm; (slits: 2.5; integration time: 0.25s). Fluorescence titration of the ligand **1** ($c = 5 \cdot 10^{-6} \text{ mol} \cdot 1^{-1}$) was carried out by addition of microliter amounts of standard solutions of [PdCl₂(C₆H₅CN)₂] ($c = 5 \cdot 10^{-4} \text{ mol} \cdot 1^{-1}$) in THF. All the spectra are concentration uncorrected. Other metal salts like Hg(ClO₄)₂·xH₂O, AgBF₄, Pb(ClO₄)₂·3H₂O, Cu(BF₄)₂·6H₂O, Ni(BF₄)₂·6H₂O, or other platinum-group metal ions such as Rh³⁺ ([RhCl₆]³⁻) and Pt⁴⁺ ([PtCl₆]²⁻) were also titrated and no fluorescence enhancement of **1** with these cations were observed. Even in the presence of a fivefolded excess of these cations, the fluorescence signal of **1** does not changed. In a solution of THF only PdCl₂ forms chelate complexes with **1**.

Lifetime measurements were performed with an FL920 fluorimeter (Edinburgh Instruments, Livingston, UK). A frequency doubled titanium sapphire laser system (Tsunami 3960; Spectra Physics, Mountain View, USA) set at 390 nm was used as the excitation light source. The original repetition rate of 80 MHz was reduced to 500 kHz with a pulse picker (Pulse Select; APE, Berlin, Germany). Fluorescence was detected with a multichannel plate (ELDY EM1-132/300, Europhoton, Berlin, Germany), providing a time response of B100 ps. The percentage was obtained from: for triple exponential decay, $I_{\rm f} = A + B_1 \cdot e^{(-t/\tau_1)} + B_2 \cdot e^{(-t/\tau_2)} + B_3 \cdot e^{(-t/\tau_3)}, f(\tau_1) = B_1/(B_1 + B_2 + B_3)[\%]$.

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Fig. 6 Fluorescence decay profiles of $\mathbf{1}$ (·), $c(\mathbf{1}) = 5 \times 10^{-6}$ M, in the presence of 1 (·) and 2 equiv. (·) PdCl₂ in THF at $\lambda_{ex} = 390$ nm. Emission monitored for $\mathbf{1}$ at 590 nm and for PdCl₂-complexes at 430 nm.

5. Theoretical

Optimized geometries were computed for the free ligand **1** and for the complexes [PdCl₂(**1**)] and [(PdCl₂)₂(**1**)]. All calculations were carried out using the Gaussian03 ⁴ program package. The B3LYP ⁵ functional and a CEP-31G ^{6,7,8} basis set with polarization functions on C,N,S and Cl were employed. This level of theory was found to be appropriate for the investigated class of compounds in earlier calculations ⁹. The excitation energies and corresponding oscillator strengths are computed by means of time dependent density functional theory¹⁰ using the same basis set and functional as for the ground state calculations. For the free ligand **1** two different conformers were investigated.

1. Conformer S: Here, the CN-groups of the thiomaleonnitril-units point in the same directions.

2. Conformer A: In this case, the CN-groups of the thiomaleonnitril-units point in opposite directions.

These structures and their electronic energies are shown in Fig. 7 They were the starting points for the optimization of the Pd-complexes [PdCl₂(1)] (**S1Pd**, **A1Pd**) and [(PdCl₂)₂(1)] (**S2Pd**, **A2Pd**). As one can see **A** and **S** and the corresponding complexes **S1Pd**, **S2Pd** and **A1Pd**, **A2Pd** differ only by a few mE_h (1 mE_h = 2.625 kJ/mol). However, given the accuracy of the electronic structure method and the experimental findings for similar compounds (see

⁴ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, et al., Gaussian 03, revision c.02, gaussian, Inc., Wallingford CT, 2004.

⁵ A. D. Becke, J. Chem. Phys., 1993, **98**, 5648.

⁶ W. Stevens, H. Basch and J. Krauss, J. Chem. Phys., 1984, **81**, 6026.

⁷ W. J. Stevens, M. Krauss, H. Basch and P. G. Jasien, Can. J. Chem., 1992, **70**, 612.

⁸ T. R. Cundari and W. J. Stevens, J. Chem. Phys., 1993, **98**, 5555.

⁹ T. Schwarze, H. Müller, C. Dosche, T. Klamroth, W. Mickler, A. Kelling, H.-G. Löhmannsröben, P. Saalfrank and H.-J. Holdt, *Angew. Chem. Int. Ed.*, 2007, **46**, 1671.

¹⁰ M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, J. Chem. Phys., 1998, 108, 4439.

e.g. 11), it should be reasonable to assume that **A** and the corresponding complexes are the more favorable structures.



Fig. 7 Shown are the optimized structures for the investigated conformers of the free ligand 1 (top) and the corresponding structures of the complexes $[PdCl_2(1)]$ (middle) and $[(PdCl_2)_2(1)]$ (bottom).

¹¹ A. Spannenberg, H.-J. Holdt, K. Praefcke, J. Knopf and J. Teller, *Liebigs Ann.*, 1996, 1005.

5.1. Spectra

The calculated spectra are shown in Fig. 8 for the conformers of the free ligand and the corresponding complexes. The spectra are computed from the oscillator strengths f_i and wave numbers \tilde{v}_i by "Gaussian broadening" ($\sigma = 700 \text{ cm}^{-1}$):

$$\epsilon(\tilde{v}) = \sum_{i} \frac{f_i}{\kappa} \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\tilde{\nu}-\tilde{\nu}_i}{\sigma}\right)^2}$$

κ is given as:

$$\kappa = \frac{4m_e c^2 \epsilon_0 \ln 10}{N_A e^2} = 4.318998 \cdot 10^{-10} \text{mol m}^{-1}$$

In the spectra one can see strong peaks around 340 nm similar as in Ref. 9, which lose intensity upon complexation. Here, we find an excitation wave length of 343.7 nm for **S** and 335.9 nm for **A**. The excited states are dominated by HOMO-3 to LUMO+2 transition for **S** and **A**. This transition corresponds to a charge transfer from the sulfur atoms to the maleonitrile unit. The orbitals are shown in Fig. 9 for the conformer **A**.

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Fig. 8 Shown are the oscillator strengths and the calculated UV/vis absorption spectra for the conformers of the free ligand 1 (black lines) and the corresponding complexes $[PdCl_2(1)]$ (red lines) and $[(PdCl_2)_2(1)]$ (green lines) (top: **S**, **S1Pd**, **S2Pd**, bottom: **A**, **A1Pd**, **A2Pd**).



Fig. 9 Shown are the HOMO-3 and LUMO+2 for the conformer A of the free ligand 1.