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Highly fluorescent and electroactive molecular squares containing perylene bisimide ligands

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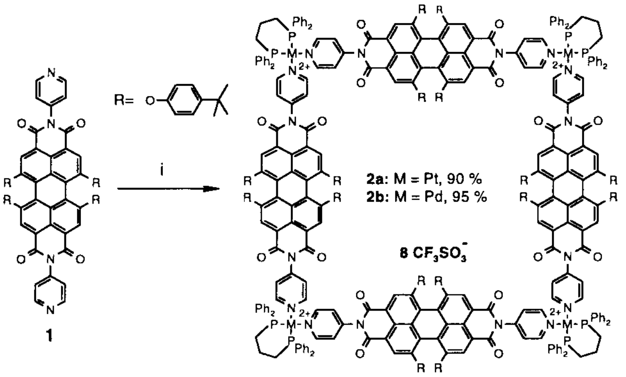
Large functional molecular squares have been assembled with ditopic perylene bisimide bridging ligands and Pt(II) and Pd(II) phosphine corner units and their optical, electrochemical and spectroelectrochemical properties have been studied.

Interest in functional supramolecular assemblies[1] has been triggered by examples from nature like the light harvesting system (LHS) in purple bacteria.[2] The supramolecular functionality of this natural assembly is realized by chlorophyll molecules organized in cyclic arrangements which control the electronic coupling of the dye molecules and allow accommodation of the reaction center of photosynthesis within the largest ring of LHS.[2] A straightforward access to cyclic structures in high yields was introduced by Fujita and Ogura[3] and Stang and Olenyuk[4] *via* the concept of molecular squares using ditopic bridging ligands and *cis*-coordinating square planar Pt(II) or Pd(II) corners. Some very interesting examples have been reported based on pyridyl-substituted porphyrin ligands,[5] where functionality is introduced by the ligand but porphyrin fluorescence is quenched upon metal complexation. Here, we report on a new ligand based on perylene tetracarboxylic acid bisimides[6,7] which exhibits fluorescence quantum yields Φ_F near 100%[6] as well as redox activity[8] and which conserves these properties in the metal-assembled state: a giant photo- and redox-active molecular square (metal–metal diagonal *ca.* 3.4 nm).

The perylene ligand **1** was synthesized in 66% yield by condensation of the corresponding perylene bisanhydride[7] with 4-aminopyridine in quinoline with catalytic amounts of zinc(II) acetate. The ligand exhibits an intense absorption band at λ_{max} = 585 nm and red fluorescence at λ_{max} = 618 nm with Φ_F = 0.94 for **1** in chloroform.[9]

Equimolar mixing of ditopic perylene ligand **1** with dpppM(OTf)$_2$ [M = Pt(II) or Pd(II), dppp = 1,3-bis(diphenylphosphino)propane; OTf = $CF_3SO_3^-$] in CH_2Cl_2 leads exclusively to the formation of molecular squares **2a**,**b** in 90 and 95% isolated yield, respectively (Scheme 1). The squares were characterized by elemental analysis, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and electrospray mass spectrometry (ESI–MS) (**2a**).† In the ^{31}P{^{1}H} NMR spectra of **2a**,**b** only one singlet is observed owing to the high symmetry of the squares, additionally there are Pt-satellites resulting from ^{195}Pt–^{31}P spin–spin coupling in the spectrum of **2a**. A typical change in chemical shifts of the phosphorus nuclei of *ca.* 10 ppm results upon complexation with **1**.[10] The ^{1}H NMR spectra show only a single set of signals for the ligand **1** and the dppp moiety with significant changes in the chemical shifts of the α- and β-pyridyl protons (*ca.* 0.3 ppm) owing to metal complexation.[10] In the ESI–MS of **2a** (acetone solution) we observed signals at *m/z* 2575.0 which we assign to the M−3OTf species with +3 charge state (separation of peaks by 1/3 mass unit) which corresponds to a molecular mass of 7725 for the square minus three triflate anions in excellent agreement with the calculated mass of 7724.89 ($C_{409}H_{360}N_{16}O_{47}F_{15}P_8S_5Pt_4$). Furthermore, we observed signals at *m/z* 1894, 1485 and 1213 which we assign to $(M-4OTf)^{4+}$, $(M-5OTf)^{5+}$ and $(M-6OTf)^{6+}$ species (THF–ethyl acetate solution). The less stable corresponding Pd-square **2b** has not, as yet, been characterized by the ESI–MS technique.



Scheme 1 *Reagents and conditions:* i, dpppM(OTf)$_2$, CH_2Cl_2, 24 h, 20 °C.

The optical and electrochemical properties of the perylene ligand **1** remain almost unchanged upon formation of the complexes **2**. We ascribe this to the fact that in perylene tetracarboxylic acid bisimides, the imide substituents have only a small electronic coupling to the HOMO and LUMO of the perylene chromophore.[8,11] Therefore, the chromophoric perylene unit is largely decoupled of the binding site and only small bathochromic shifts of $\Delta\lambda$ = 5–7 nm in the absorption and emission spectra are observed upon complexation. The absorption maximum of **2a** is located at λ_{max} = 591 nm, the emission occurs at 625 nm. An even more important consequence is negligible quenching of the perylene fluorescence in these complexes with Φ_F (**2a**, $CHCl_3$) = 0.88.[9]

The ligand **1** and platinum complex **2a** exhibit reversible electrochemistry which was investigated by cyclic voltammetry in CH_2Cl_2. **1** displays two, reversible reductions at potentials of −1.08 and −1.23 V (*vs.* Fc/Fc$^+$), but oxidation is irreversible causing adsorption of **1** on the platinum electrode. The molecular square **2a** shows two reversible waves in the reductive cycle at similar potentials (−1.01, −1.14 V *vs.* Fc/Fc$^+$) but the oxidative cycle, in contrast to **1** shows a reversible wave at +0.93 V, probably as a consequence of the pyridyl nitrogen lone pairs which are now blocked by platinum-complexation (Fig. 1). The electrochemical studies of the palladium complex **2b** revealed a more complicated behavior displaying an irreversible reduction at $E < -1.15$ V which we attribute to electron transfer processes involving the Pd(II) corners.

A closer insight into the electrochemical processes was gained by spectroelectrochemical investigations of **2a** and **1**. By increasing the potential in a stepwise manner to the first reduction wave of **2a** (−1.01 V) the absorption bands of the perylene bisimide chromophores at 591 nm decrease while three bands in the UV–VIS–NIR appear with a maximum absorption at 791 nm [Fig. 2(a)]. Based on identical spectroscopic changes observed for the free perylene bisimide ligand **1**, we assign these optical transitions to perylene bisimide radical anionic species. After a further increase of the potential to the second reduction

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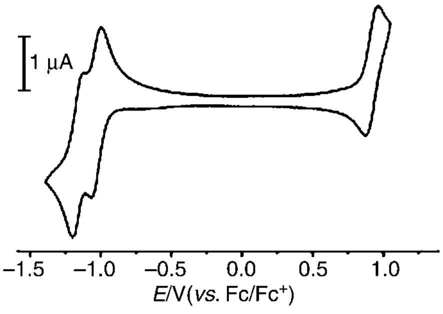

Fig. 1 Cyclic voltammogram of perylene–platinum square **2a** in CH_2Cl_2; scan rate 100 mV s^{-1}. Working electrode: Pt disc, auxiliary electrode: Pt wire, reference electrode: Ag/AgCl; concentration **2a** = 2.5×10^{-4} M; supporting electrolyte NBu_4PF_6 (0.1 M).

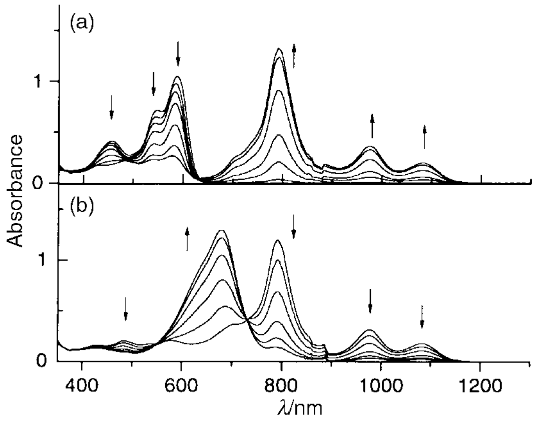

Fig. 2 Spectroelectrograms of perylene–platinum square **2a** in CH_2Cl_2 with NBu_4PF_6 (0.1 M) as supporting electrolyte. Working electrode: Pt disc; auxiliary electrode: Pt wire; reference electrode: Ag/AgCl; concentration **2a** = 1.4×10^{-4} M. Stepwise increase of the applied potential to radical anionic perylene species (a) and to dianionic perylene species (b).

wave of **2a** (−1.14 V) the perylene radical anion bands disappear completely whereas a broad and intense band appears, with a maximum absorption at 679 nm [Fig. 2(b)], corresponding to dianionic perylene bisimides. Oxidation to the radical cationic state results in less pronounced spectral changes in the visible but new broad bands appear in the NIR at 809, 908 and 1225 nm. The distinct isosbestic points in the absorption spectra for all redox couples confirm the reversibility of all oxidation and reduction processes. Therefore, we conclude that (i) the redox processes take place exclusively at the perylene ligands with the Pt(II) corner units being inert in the applied potential range and acting solely as structural building blocks, (ii) the perylene ligands assembled in the square do not interact with one another even in a charged state, and (iii) each perylene ligand in the square is reduced and oxidized at the same time at the given potentials.[12]

In summary, we report on a new functional ditopic perylene ligand **1** which has been used to construct nanosized molecular squares **2** with Pt(II) and Pd(II) phosphine corner units. The optical and electrical properties of the ligands are conserved in the metal-assembled state **2a** which shows a fluorescence quantum yield of almost unity and multiple, fully reversible redox couples. The giant inner volume of nanosquares **2** seems ideal to accommodate large functional guest molecules for studies on redox and photocatalytic processes.

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Notes and references

† *Selected data for* **2a**: mp > 330 °C. ^1H NMR ($CDCl_3$, 500 MHz), δ 9.13 (br s, 16H), 8.12 (s, 16H), 7.69 (br s, 32H), 7.40 (m, 32H), 7.32 (m, 16H), 7.20 (d, 32H, J 8.4 Hz), 7.09 (d, 16H, J 5.9 Hz), 6.77 (d, 32H, J 8.4 Hz), 3.29 (br s, 16H), 2.20 br s, 8H), 1.24 (s, 144H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 85% H_3PO_4, 202 MHz), δ −15.11 (s). UV–VIS(CH_2Cl_2), λ (ε) 591 (217000), 550 (135000), 459 nm (72000 dm^3 mol^{-1} cm^{-1}). $\lambda_{\mathrm{em,\,max}}$($CH_2Cl_2$) 625 nm. MS (ESI, acetone) Calc. (M−3OTf)$^{3+}$ *m/z* 2575.7. Found 2575.0. Found: C, 59.29; H, 4.59; N, 2.54; S, 3.03. $C_{412}H_{360}N_{16}O_{56}F_{24}P_8Pt_4S_8 \cdot 8H_2O$ requires C, 59.50; H, 4.56; N, 2.69; S, 3.08%.

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