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Assembling Phthalocyanine Dimers through a Platinum(II) Acetylide Linker

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Dedicated to Professor Michael Hanack on the occasion of his 80th birthday

Abstract: Phthalocyanine (Pc) dimers connected through *trans*-platinum(II) diacetylide linkers have been prepared by reaction of the corresponding ethynylphthalocyanines with *trans*-bis(triethylphosphine)platinum(II) chloride. Special emphasis was placed on the analysis of the ground- and excited-state features of these compounds in

relation to butadiyne-bridged Pc dimers and the corresponding monomers. Both Zn^{II}-containing Pc dimers exhibit long-lived triplet excited states.

Keywords: acetylides • fluorescence • photochemistry • phthalocyanines • platinum

The insertion of σ -bonded *trans*-platinum(II) diacetylide spacers decoupled the two Pc groups and led to an appreciable acceleration (by a factor of up to 10) of the radiative and nonradiative decay rate of the singlet and triplet excited states.

Introduction

The ubiquitous structure of porphyrins has fascinated scientists during the last century owing to its essential role in a variety of biological events. Most of these processes imply electronic and/or photonic collaboration between a defined number of these chromophores, for example, in light-harvesting antenna systems, whereas others are mediated by the interaction between porphyrins and other electroactive systems (reaction centers).

Phthalocyanines (Pcs) and porphyrins possess analogous photophysical and redox properties. The latter fact has rendered these types of macrocycles attractive targets for incorporation in biomimetic systems^[1] and artificial photosynthetic materials.^[2] Their potential applicability in sensing,^[3] mag-

netic^[4] and optoelectronic devices,^[5] together with their utility as catalysts^[6] or photosensitizers,^[7] however, is more due to their differential optical and electronic features than their similarities. Thus, porphyrins exhibit their main absorption in the blue region, whereas the bare Pc molecule shows strong absorption cross-sections in the red region of the electromagnetic spectrum.^[8] Moreover, the position of these absorption bands can be fine-tuned through the introduction of different central metal ions and by selecting the appropriate peripheral functional groups. Although the use of red absorbers for some of the above-mentioned purposes can be desirable, the strong absorptions of these materials at wavelengths higher than 650 nm are imperative for biomedical applications, such as photodynamic therapy (PDT) or fluorescent contrast imaging.

We have devoted considerable effort to constructing a wide variety of Pc-based multimacroscopic assemblies, through the utilization of different types of linkers (in terms of chemical composition and geometrical features) to study the electronic interactions between chromophores and the new properties arising from these junctions.^[9] We have also prepared a large number of Pc-containing electron-donor–acceptor hybrids, in which the complementary electroactive units are of a diverse nature and/or redox character (ferrocene, trisbipyridine complexes, subphthalocyanines, peryleneimide,^[10] porphyrin,^[11] quinone,^[12] fullerene, or carbon nanotubes).^[13] In these cases varying solely the type of linker within the same donor–acceptor motif, afforded hybrids that exhibited dissimilar physicochemical features.^[10–13] Thus, for each array, the selected connection mode between units provides a unique shape, dimension, and supramolecular organization. These parameters, in conjunction with the nature of the chemical bonding, govern the efficiency of electronic or photonic coupling between the electroactive units both in the ground and excited states. As an illustrative

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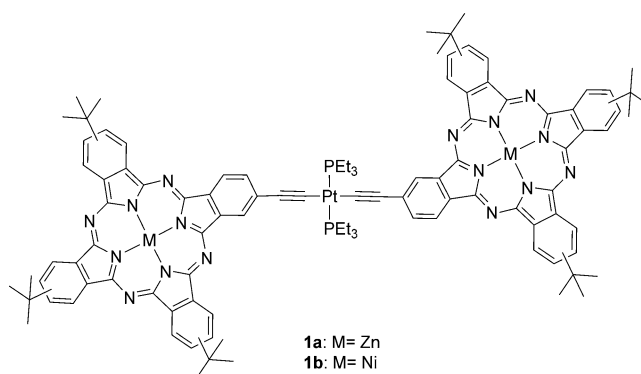
example, we have prepared an assortment of Pc–fullerene ensembles that are connected by a variety of covalent and supramolecular bridges, which bring about manifold (through-bond and/or through-space) Pc–C₆₀ interactions and we have studied their ability to generate radical ion pair states upon photochemical excitation.^[13] Although all of these systems were able to produce electron-transfer events, the nature of Pc–C₆₀ communication greatly influenced the efficiencies in terms of, for instance, charge-separated-state lifetimes.^[13] Therefore, in the design of multicomponent Pc-based functional materials, selecting the right linker may be as powerful as choosing the appropriate motif itself.

Pcs endowed with acetylene functional groups have extensively been used as precursors of higher-order molecular materials.^[9a] The utility of the alkynyl group arises from its physical and chemical features, namely, its linear geometry, structural rigidity, extended π -electron delocalization, flexible reactivity,^[14] and ability to be used in a variety of transition-metal-catalyzed chemical reactions that allow the facile assembly of complex, multicomponent systems. In addition, the ethynyl function is able to interact with metal centers through p_{π} – d_{π} overlap, and hence, it has been used as a building block in the construction of carbon-rich, metal-containing materials with potential applications in electrical conductivity,^[15,16] luminescence,^[17] and liquid-crystal (LC) technologies.

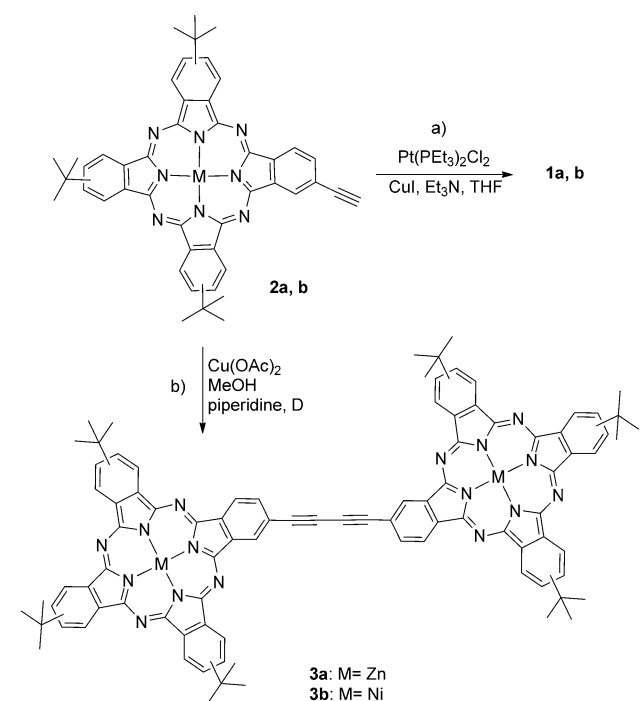
Despite growing interest in alkynyl metal compounds, examples of platinum complexes containing σ -bonded ethynylporphyrins are scarce^[18] and, to the best of our knowledge, the platinum(II) acetylide bridge has not been previously utilized in the assembly of Pc systems. The platinum(II) diacetylide moiety may provide additional properties to the array because heavy atoms, such as platinum, induce strong spin-orbit coupling (SOC), and give rise to systems that exhibit rapid intersystem crossing and high yields of the triplet excited state. Fluorescent and phosphorescent materials attract commercial and scientific interest because of their potential applications in optoelectronic devices, such as light-emitting diodes (LEDs), optical power limiters (OPL), lasers, photocells, and large-area flexible displays. Herein, we report the synthesis, as well as the chemical and photophysical characterization of two Pc dimers **1a** and **1b**, both of which contain a platinum(II) diacetylide bridge. We also present results from electrochemical studies carried out to determine whether this linker brought about electronic coupling between the two Pc halves.

Results and Discussion

Synthesis: The Pc ligands were endowed with *tert*-butyl groups because this kind of functionalization usually provides complexes that are soluble in organic solvents and reduces aggregation, thus facilitating the purification and chemical characterization of the compounds. The σ -bonded platinum(II) acetylide dimers **1a,b** were synthesized in moderate yield ($\approx 65\%$) by the coupling reaction of *trans*-[PtCl₂–



(PEt₃)₂] with the corresponding ethynylphthalocyanines **2a,b**.^[19] The use of CuI as a catalyst led to enhanced yields of about 75% (Scheme 1a).



Scheme 1. Synthesis of dimers **1a,b** and **3a,b**.

Butadiyne-bridged Pc dimers **3a,b** were also prepared and were used as reference compounds to check the effect of the σ -bonded Pt^{II} ion on the electronic properties of dimers **1a,b**. Thus, the oxidative coupling of **2a,b**, according to a reported procedure, afforded the desired complexes **3a,b** in moderate yields (Scheme 1b).^[19]

All new compounds were characterized by spectroscopic techniques, such as ¹H NMR, ³¹P NMR, IR, and UV/Vis spectroscopy and MS (MALDI-TOF) spectrometry. Dimers **1a,b** maintain the *trans* (P–Pt–P) configuration of [PtCl₂–(PEt₃)₂], as evidenced by their ³¹P NMR spectra. Hence, both complexes displayed a singlet resonance at $\delta = 10.7$ and 11.0 ppm, respectively, and platinum satellite signals with *J*–

(Pt,P) = 2390 and 2345 Hz, respectively; this is characteristic of the *trans* geometry.^[20] In addition, compounds **1a,b** exhibited molecular ions $[M]^+$ in MS (MALDI-TOF) spectra at 1964–1977 and 1952–1964, respectively. ^1H NMR spectroscopic analysis provided very broad signals, indicating strong aggregation in solution and IR spectroscopy showed the $\nu_{\text{C}\equiv\text{C}}$ stretching band at 2093 and 2096 cm^{-1} , respectively, at similar frequencies, but considerably more intense than those corresponding to monomers **2a,b**.

Optical studies: Additional structural information could be gathered from optical spectroscopy analyses of **1–3**. Although the high-energy region showed several optical transitions that remained essentially the same on going from monomer **2a,b** to any of the dimers **1a,b** and **3a,b**, the low-energy region looked significantly altered. Thus, the UV/Vis spectra of the butadiynyl-connected dimer **3a** in chloroform (Figure 1) displayed a 10 nm redshifted and split Q band rel-

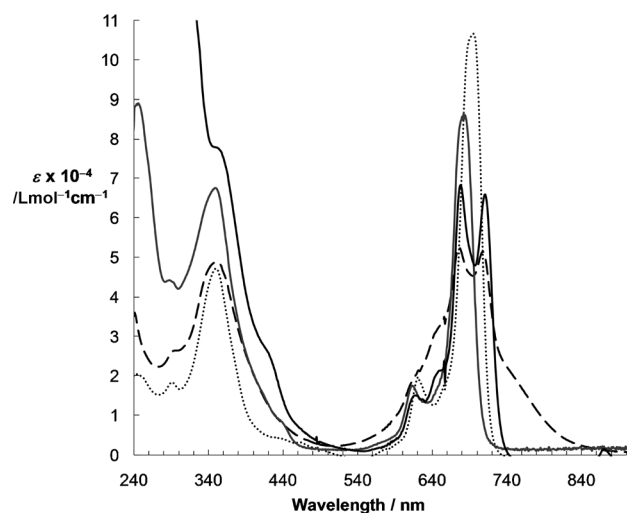


Figure 1. UV/Vis spectra of **1a** (dotted line) **2a**, (grey solid line), and **3a** (dashed line) in chloroform and **3a** in pyridine (solid line).

ative to the corresponding monomer **2a**.^[21] The considerable broadening of this band indicated aggregation, which was noticeably reduced upon the addition of pyridine.

The large splitting of the Q band in compound **3a** (32 nm) arose either from a strong electronic coupling between the two macrocycles,^[12a] or from the A_3B constitution of the Pc halves, both of which possess a symmetry that was considerably reduced relative to an identically substituted A_4 -Pc (i.e. tetra-*tert*-butylphthalocyanine).^[19] The formation of aggregated species in solution should be responsible for the two broad blue- and redshifted bands, respectively, exhibited by **3a**. These aggregation bands completely disappeared when the spectrum was recorded in neat pyridine; the extinction coefficient of the monomeric Zn-Pc absorption increased at the expense of these bands.

Dimer **3b** also showed a broad Q band (Figure 2) in chloroform, in addition to a blueshifted aggregation band,

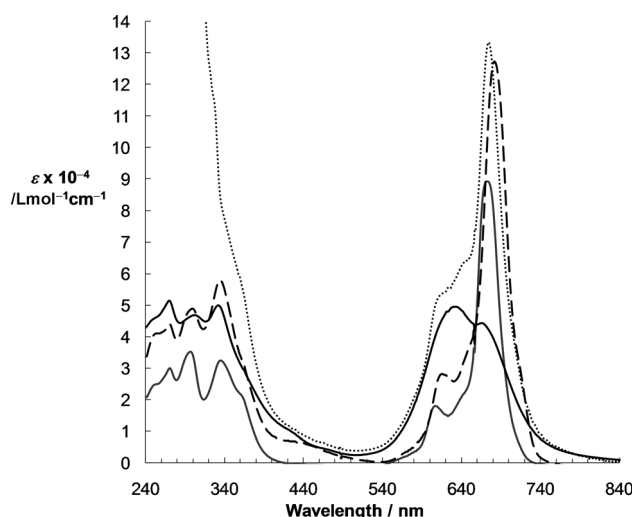


Figure 2. UV/Vis spectra of **1b** (dashed line) **2b**, (grey solid line), **3b** (solid line) in chloroform and **3b** in pyridine (dotted line).

which appeared at 633 nm and indicated the formation of H aggregates.^[22] As for the zinc derivative, the addition of pyridine resulted in a drastic reduction of the high-energy aggregation band, whereas the dominant absorption corresponding to the monomer appeared at 677 nm (Figure 2). We, therefore, concluded that the attachment of the two Pcs through a butadiyne bridge had a negligible effect (2 nm redshift) on the monomeric Q-band energy and shape.

A comparison with the optical spectra of the σ -bonded platinum(II) acetylide dimers **1a,b** revealed notable differences. Thus, the UV/Vis spectra of these complexes displayed single Pc Q bands (at 695 and 682 nm) that were 13 and 9 nm redshifted, respectively, relative to monomers **2a,b** (Figures 1 and 2). Moreover, in the transition from **2a,b** to **1a,b** the Q band showed no indication of broadening or splitting (with a full-width at half-maximum in the order of 30 nm in all the four cases). In summary, the optical spectroscopy of compounds **1a,b** and **3b** suggested that the two Pc halves are essentially decoupled in the ground state.^[23] This is not surprising for bisphthalocyanines **1a,b** because the Pt^{II} ion often reduces or even disrupts conjugation.^[18b,24] A scarce involvement of the platinum d orbitals in the HOMO of related porphyrin dimers has been proposed to explicate the decrease in the π -electronic delocalization upon insertion of the Pt^{II} ion.^[18b] On the other hand, the lack of electronic communication between the two chromophores in the butadiyne-connected Ni dimer **3b** could be interpreted as evidence that the two Pcs lie approximately orthogonal to each other, as previously suggested for related porphyrin dimers.^[25] With respect to compound **3a**, it is impossible to determine by UV/Vis spectroscopy whether the observed Q-band splitting arises from the reduced symmetry of the A_3B macrocycles or the electronic coupling between the two Pc subunits.^[26] Electrochemical studies were deemed necessary to reach more definitive conclusions.

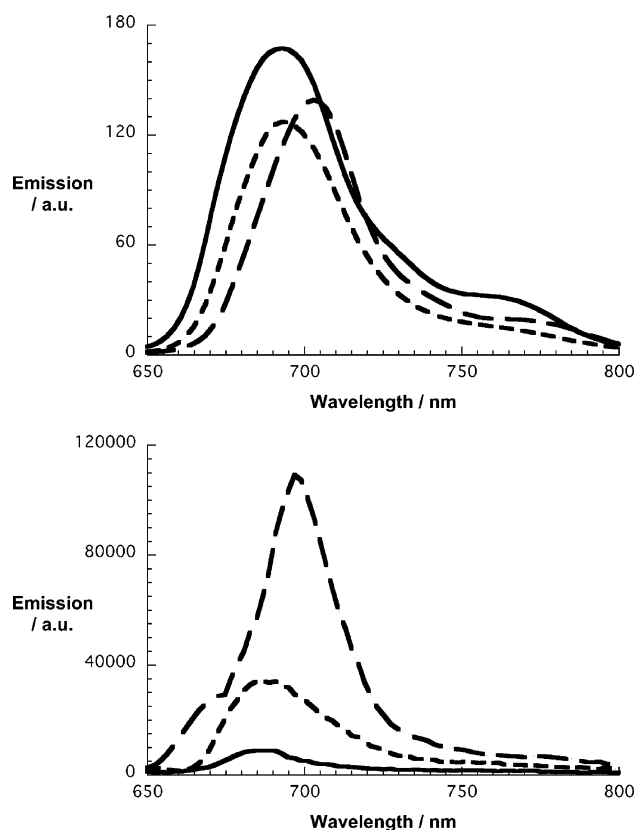


Figure 3. Top: Fluorescence spectra of **2a** (solid line), **3a** (long dashed line), and **1a** (short dashed line) in benzonitrile with the same optical absorption of 0.2 at 678 nm at room temperature. Bottom: Fluorescence spectra of **2b** (long dashed line), **3b** (short dashed line), and **1b** (solid line) in benzonitrile with the same optical absorption of 0.2 at 663 nm at room temperature.

Steady-state fluorescence spectroscopy analyses showed a similar trend (Figure 3). In particular, an overall broadening was discernable for **3a** and **3b** in comparison with **1a** and **1b**, as well as with the Zn–Pc and Ni–Pc monomers **2a,b**. The fluorescence maxima were located at 690 (**2a**), 690 (**1a**), and 705 nm (**3a**). The fluorescence quantum yields were, however, striking. For example, the quantum yields of dimers **3a** and **1a** were quenched with values of 0.037 and 0.035, respectively, relative to the quantum yield of monomer **2a** (0.27). In other words, the butadiynyl linker in **3a** and the platinum diacetylide bridge in **1a** both seem to induce an equally fast deactivation (by a factor of 10) of the photoexcited Zn–Pc complex. Time-resolved fluorescence spectroscopy experiments confirmed the latter hypothesis: Fluorescence lifetimes of 0.35 and 0.36 ns were found for **3a** and **1a**, respectively, relative to a lifetime value of 2.8 ns for the Zn–Pc monomer **2a**.

Likewise, inspection of the fluorescence data for the Ni–Pc compounds indicated an appreciable fluorescence quenching for **3b** (0.0005)^[27] and **1b** (0.0001). The corresponding reference value for **2b**, however, was 0.003, that is, two orders of magnitude lower than that of the Zn–Pc monomer **2a**. It is notable that the intrinsically low fluores-

cence quantum yield of NiPcs allowed us to dissect the differences between the butadiyne and platinum acetylide linkers. As expected, the presence of the platinum diacetylide linker had a more profound impact on the fluorescence emission spectrum of the dimer. No detectable fluorescence was seen in the time-resolved experiments with either of the Ni–Pc compounds, which suggested that the corresponding deactivation was faster than the time resolution of our apparatus (approximately 100 ps).

We subsequently tested all of the different systems by transient absorption spectroscopy in benzonitrile/pyridine (1:2). For monomer **2a** we noted that, upon excitation at 656 nm, the singlet–singlet spectrum (featuring maxima at 485/595/635/825 nm and minima at 615/685 nm; Figure S9 in the Supporting Information) is instantaneously formed. In line with the absorption spectra, the differential absorption changes were rather sharp, especially in the minima. The singlet excited state was long-lived and underwent a slow intersystem crossing (3.0 ns) to yield the corresponding triplet manifold. The latter was characterized by a maximum at 490 nm and minima at 615/685 nm. Conversely, the differential absorption spectra for the butadiyne dimer **3a** included rather broad signals, with maxima at 505, 805, 845, and 970 nm and a minimum at 680 nm (Figure S10 in the Supporting Information). The intersystem crossing to the Zn–Pc triplet excited state was much faster (0.68 ns) than that in the corresponding monomer **2a**. Finally, we should mention that in the singlet–singlet absorption spectra of the platinum diacetylide dimer **1a**, sharp maxima at 500, 590, 640, 810, 850, and 975 nm, as well as sharp minima at 620, 685 and 700 nm (Figure 4), were observed. In this case, the intersystem crossing was extremely fast (0.3 ns) and comparable to the fluorescence lifetime. In both of the systems, that is, **2a** and **1a**, we noted that the triplet excited state was formed with its characteristic absorption at 505 nm. The triplets decay on the nano- and microsecond timescale with lifetimes of 46 (**3a**) and 12 μ s (**1a**).

For the Ni–Pc monomer **2b**, maxima at 520 and 705 nm were associated with the singlet excited state, whereas minima evolved at 605 and 670 nm (Figure S11 in the Supporting Information). The triplet excited state, on the other hand, exhibited a single maximum at 500 nm and two minima at 615 and 680 nm. Similarly to the fluorescence assays, the singlet excited state was short-lived and showed intersystem crossing to the triplet state. In fact, the intersystem crossing dynamics are best fit by a biexponential fitting function with lifetimes of 9.9 (85 %) and 52 ps (15 %). Neither **3b** nor **1b** revealed any significant deviations from the aforementioned behavior (Figure 5 and Figure S12 in the Supporting Information). Spectroscopically, both the singlet and the triplet excited-state properties are nearly identical to those seen for the Ni–Pc monomer **2b**. Kinetically, two lifetimes emerged with values that tended to be slightly shorter for the butadiyne dimer **3b** (8.2 and 31.9 ps), relative to the platinum diacetylide dimer **1b** (11.8 and 66.4 ps). For the Ni–Pc systems, the triplet excited states decayed with lifetimes of 55 (**2b**), 50 (**3b**), and < 10 ns (**1b**).

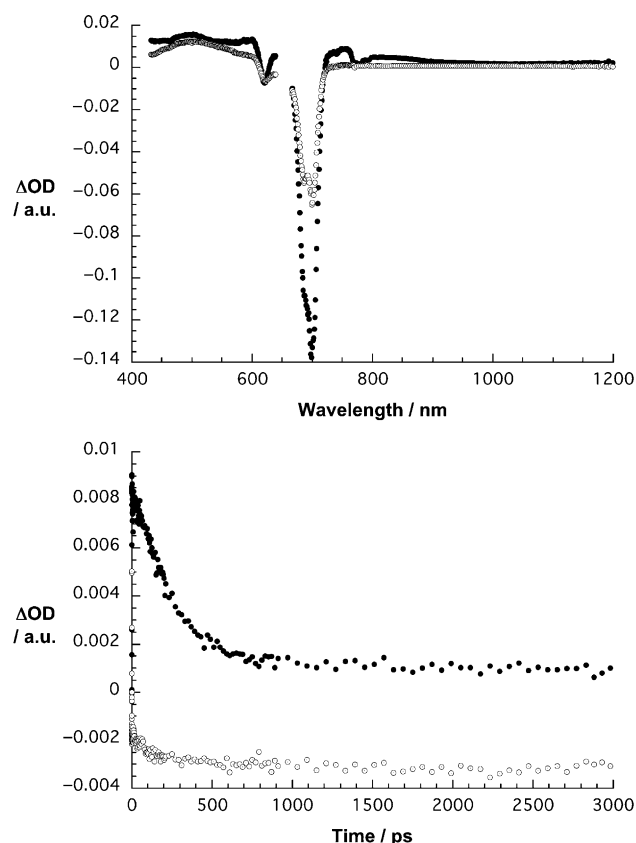


Figure 4. Top: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (650 nm) of **1a** in benzotrile/pyridine (2:1) with time delays of 1.1 (●) and 1272 ps (○) at room temperature. Bottom: Time-absorption profiles of the spectra shown above at 750 (●) and 615 nm (○) monitoring the intersystem crossing.

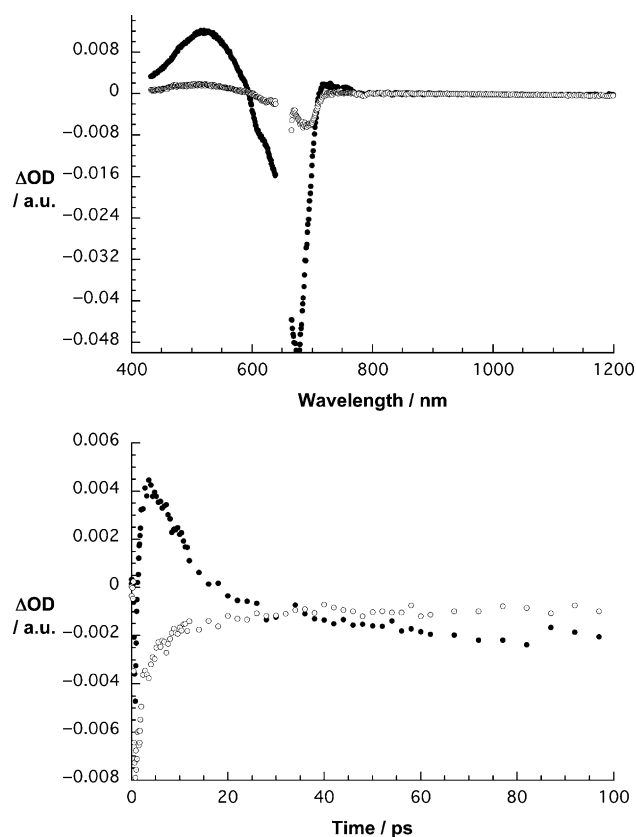


Figure 5. Top: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (650 nm) of **1b** in benzotrile/pyridine (2:1) with time delays of 1.2 (●) and 832 ps (○) at room temperature. Bottom: Time-absorption profiles of the spectra shown above at 710 (●) and 610 nm (○) monitoring the intersystem crossing.

Electrochemical studies: Cyclic (CV) and square-wave voltammetry (SWV) measurements were performed in THF (**1a,b–3a,b**) and in CH_2Cl_2 (**1b–3b**). Relevant data are compiled in Table 1. Electrochemical reduction of the Zn-containing Pc monomer **2a** and dimers **1a** and **3a** afforded two completely reversible peaks with $\Delta E_p \approx 80$ mV ($\nu = 0.1 \text{ V s}^{-1}$) relative to the “model” compound Fc^+/Fc^* under the same conditions and $I_{pa}/I_{pc} \approx 1$ (Figure 6). Dimers **1a** and **3a** showed

Table 1. Electrochemical reduction and oxidation data recorded in THF (data recorded in CH_2Cl_2 are given in parentheses). $E_{1/2}$ (from CV and SWV at room temperature) values are given in V versus decamethylferrocene (Fc^+/Fc^*). Under the actual experimental conditions, $E_{1/2}$ ($\text{Fc}^{2+}/\text{Fc}^*$) is +0.44 and +0.55 V versus the Fc^* system in THF and CH_2Cl_2 , respectively.

	$E_{1/2}(\text{red1})$	$E_{1/2}(\text{red2})$	$E_{1/2}(\text{ox1})$	$E_{1/2}(\text{ox2})$
1a	−1.01	−1.49	0.63	0.76
2a	−0.96	−1.44	0.64	0.81
3a	−0.92	−1.39	0.61	0.83
1b	−0.91 (−0.87)	−1.39 (−1.21; −1.27) ^[a]		
2b	−0.89 (−0.82)	−1.31 (−1.15)		
3b	−0.88 (−0.82)	−1.27 (−1.24)		

[a] Wave split in CH_2Cl_2 .

no evidence of wave splitting indicative of electronic communication between the two Pc-Zn^{II} redox centers, either through the butadiyne (**3a**) or Pt^{II} diacetylide (**1a**) bridges.

The Ni-containing macrocycles **2b** and **3b** also underwent two distinct reduction processes, although complete reversibility was only attainable for monomer **2b**. In a solution of the Pt^{II} diacetylide-bridged Pc dimer **1b** in CH_2Cl_2 , however, a second reduction process took place and, thus, the overall process gave rise to two close waves ($\Delta E_{1/2} \approx 60$ mV) that could not be completely resolved, even with SWV (Figure 7). By rigorous analysis of UV/Vis and ^1H NMR spectroscopy data, we concluded that this splitting most likely arose due to the strong aggregation of compound **1b** under these conditions. In the first reduction process, adsorption was probably involved.

As seen in Table 1, butadiyne-bridged dimers **3a,b** are easier to reduce than the monomers because they possess LUMOs that are more easily accessible. When Pt^{II} was inserted, however, the trend was reversed. The effect of the solvent on half-wave potential values and the separation between the two reduction processes was also noteworthy: In CH_2Cl_2 , $E_{1/2}$ values were less negative, particularly for the second process. All Ni-containing compounds were, addi-

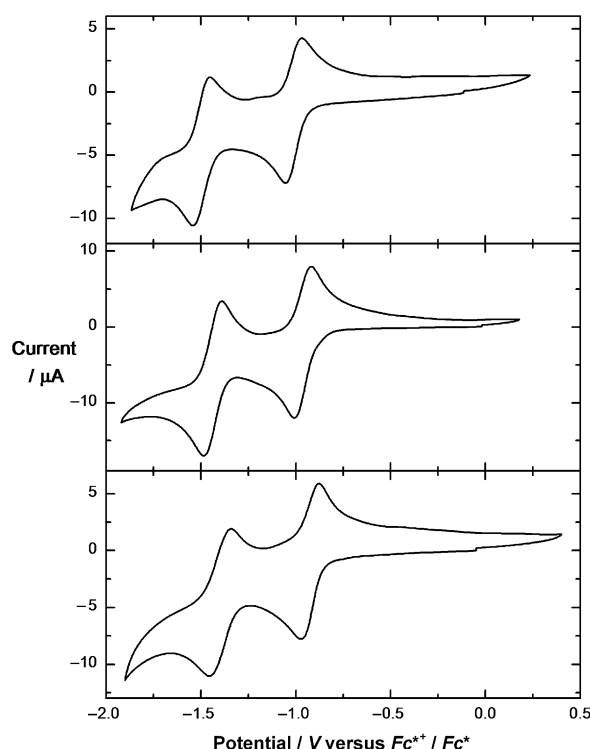


Figure 6. Cyclic voltammograms for the reduction of **1a** (top), **2a** (middle), and **3a** (bottom) in THF at room temperature and $\nu = 0.1 \text{ V s}^{-1}$ on a Pt electrode. Potential values refer to the $E_{1/2}$ value of the Fc^+ system, which was added as an internal standard after a series of experiments. The concentration of the solution of **2a** was approximately 3.5 times higher than those of **1a** and **3a**.

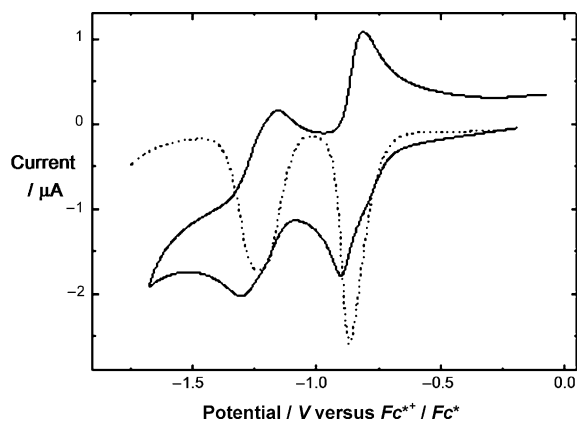


Figure 7. Cyclic (solid line) and square-wave (dotted line) voltammograms for the reduction of **1b** in CH_2Cl_2 at room temperature and $\nu = 0.1 \text{ V s}^{-1}$ (CV) or 15 Hz (SWV). Potential values refer to the $E_{1/2}$ value of the Fc^+ system, which was added as an internal standard after a series of experiments.

tionally, easier to reduce than the corresponding Zn derivatives (in THF).

The electrochemical oxidation of Zn^{II} derivatives **1a–3a** showed two peaks (Table 1) that were not completely chemically reversible (Figure 8). On the contrary, the oxidation of the Ni-containing compounds **1b–3b** was poorly defined be-

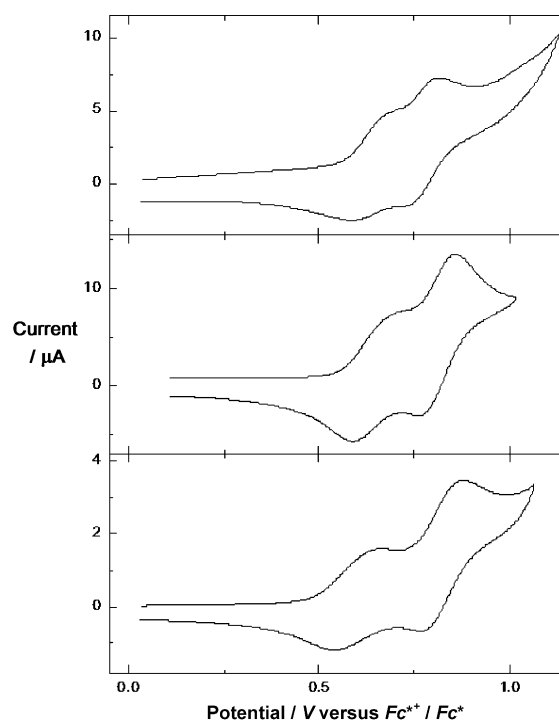


Figure 8. Cyclic voltammograms for the oxidation of **1a** (top), **2a** (middle), and **3a** (bottom) in THF at room temperature and $\nu = 0.1 \text{ V s}^{-1}$. Potential values refer to the $E_{1/2}$ value of the Fc^+ system, which was added as an internal standard after a series of experiments. The concentration of the solution of **2a** was approximately 3.5 times higher than those of **1a** and **3a**.

cause adsorption processes were involved and $E_{1/2}$ values could not be determined.

Conclusion

Herein, the first synthesis, chemical, electrochemical, and photophysical characterization of Pc dimers connected through σ -bonded *trans*-platinum(II) diacetylide spacers was reported. Analyses by UV/Vis spectroscopy, CV, and SWV indicated that the two Pc halves were electronically decoupled in these compounds. Despite the electronic decoupling of the two Pc halves, the insertion of a σ -bonded *trans*-platinum(II) diacetylide spacer induced, because of the heavy-atom effect, faster intersystem crossing for transformations from the singlet excited state to the triplet excited state and the triplet excited state to the singlet ground state. The corresponding singlet and triplet excited-state lifetimes for the zinc–Pc dimers were 0.3 ns and 12 μs , respectively, that is, triplet states with lifetimes that were longer by two orders of magnitude relative to heavy-atom-substituted Pcs, such as Ru-containing Pcs.^[28] On the other hand, the butadiyne-bridged zinc–Pc dimers gave lifetime values of 0.68 ns and 46 μs , respectively.

Experimental Section

Synthesis: UV/Vis spectra were recorded on a Hewlett–Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. MALDI-TOF spectra were recorded on a Bruker Reflex III spectrometer. NMR spectra were recorded on Bruker AC-300 and Bruker DRX-500 instruments. Column chromatography was conducted on silica gel Merck-60 (230–400 mesh, 60 Å) and Biobeads SX-1. TLC was performed on aluminum sheets precoated with silica gel 60 F₂₅₄ (Merck). Chemicals were purchased from Aldrich and used as received without further purification. Ethynylphthalocyanines **2a,b** and butadiyne-bridged dimers **3a,b** were prepared as previously reported.^[26]

Photophysics: All measurements were carried out at room temperature and all solvents used were of spectroscopic grade and were purchased from Sigma–Aldrich. Steady-state emission spectra were recorded on a Fluoro-Max 3 fluorometer built by Horiba Jobin Yvon in a 10 × 10 mm quartz cuvette. Emission lifetimes were determined with time correlated single-photon counting (TCPSC) on a FluoroLog3 emission spectrometer (Horiba Jobin Yvon) with a MCP detector (R3809U-58). For excitation, a laser diode (NanoLED 647 nm) was used. Femtosecond transient absorption studies were performed with 656 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:sapphire laser system (Clark-MXR); the laser energy was 135 nJ. Nanosecond laser flash photolysis experiments were performed with 355 nm laser pulses (Q-Switch Nd:YAG Laser, Brilliant Quantel, 1 Hz and 5 ns FWHM). Optical detection was based on a 0.5 Hz pulsed xenon lamp (XBO 450, Osram), a monochromator (Spectra Pro 2300i, Acton Research), a R928 photomultiplier tube (Hamamatsu Photonics), and a 1 GHz digital oscilloscope (WavePro7100, LeCroy). The laser power of every laser pulse was recorded by means of a bypass equipped with a fast silicon photodiode. The experiments were performed in a 5 × 10 mm quartz cuvette at room temperature and the solutions were oxygen free.

Electrochemistry: Electrochemical measurements were carried out by means of an AUTOLAB electrochemistry system in a three-electrode cell under a N₂ atmosphere in anhydrous deoxygenated solvents (CH₂Cl₂ and THF) containing 0.15 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. CV and SWV studies were carried out by using polycrystalline Pt or glassy carbon as the working electrodes, the counter electrode was a Pt gauze, and the reference electrode was a silver wire quasi-reference electrode. Fc* was used as the internal standard, and all half-wave potentials in this work refer to the Fc*/Fc couple. Under the actual experimental conditions, the E_{1/2} value of the ferrocene couple (Fc⁺/Fc) was +0.44 V versus Fc*/Fc* in THF and +0.55 V versus Fc*/Fc* in CH₂Cl₂.

General procedure for the synthesis of 1a,b: A solution of **2a,b** (0.06 mmol), CuI (0.5 mg, 3 μmol), and *trans*-[PtCl₂(PEt₃)₂] (7 mg, 10 μmol) in Et₃N/THF (1:1) was stirred under argon for 16 h at 50 °C. After evaporation of the solvent, gel permeation chromatography (Bio-Beads S-X1) was carried out with THF as the eluent. The first fraction was suspended in hexanes, filtered, and washed with hexanes and then with methanol. Finally, it was dried at 90 °C and 10^{−1} mmHg, affording **1a,b** as a green solid.

Compound 1a: Yield 75%; ¹H NMR (300 MHz, CDCl₃): δ = 9.3–7.5 (brm; arom), 2.8–2.6 (brs; -CH₂CH₃), 2.0–1.8 (brs; *t*Bu), 1.5–1.3 ppm (brs; -CH₂CH₃); ³¹P NMR (81 MHz, CDCl₃): δ = 10.7 ppm (*J*(P,P) = 2390 Hz); FTIR (KBr): $\tilde{\nu}$ = 2964, 2924, 2858 (C-H), 2093 (C≡C), 1614, 1418, 1333, 1394, 1261, 1094, 1041, 926, 748 cm^{−1}; UV/Vis (CHCl₃): λ_{max} (log ε) = 350 (4.67), 621 (4.29), 695 nm (5.03); MS (MALDI-TOF, dithranol): *m/z*: 1964–1977 [*M*]⁺.

Compound 1b: Yield 75%; ¹H NMR (300 MHz, CDCl₃): δ = 9.1–7.6 (brm; arom), 2.9–2.5 (brs; -CH₂CH₃), 2.0–1.5 (brs; *t*Bu), 1.5–1.4 ppm (brs; -CH₂CH₃); ³¹P NMR (81 MHz, CDCl₃): δ = 11.0 ppm (*J*(P,P) = 2345 Hz); FTIR (KBr): $\tilde{\nu}$ = 2956, 2870, 2094 (C-H), 2096 (C≡C), 1609, 1458, 1250, 1063, 910 cm^{−1}; UV/Vis (CHCl₃): λ_{max} (log ε) = 300 (4.69), 335 (4.76), 615 (4.45), 682 nm (5.10); MS (MALDI-TOF, dithranol): *m/z*: 1952–1964 [*M*]⁺.

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