CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200900262

Charge-Transfer State and Large First Hyperpolarizability Constant in a Highly Electronically Coupled Zinc and Gold Porphyrin Dyad

Jérôme Fortage,[a] Annabelle Scarpaci,[a] Lydie Viau,[a] Yann Pellegrin,[a] Errol Blart,[a] Magnus Falkenström,[b] Leif Hammarström,*[b] Inge Asselberghs,[c] Ruben Kellens,[c] Wim Libaers,[c] Koen Clays,*[c] Mattias P. Eng,*[d] and Fabrice Odobel*[a]

Abstract: We report the synthesis and the characterizations of a novel dyad composed of a zinc porphyrin (ZnP) linked to a gold porphyrin (AuP) through an ethynyl spacer. The UV/Vis absorption spectrum and the electrochemical properties clearly reveal that this dyad exhibits a strong electronic coupling in the ground state as evidenced by shifted redox potentials and the appearance of an intense charge-transfer band localized at $\lambda = 739$ nm in dichloromethane. A spectroelectrochemical study of the dyad along with the parent homometallic system (i.e., ZnP–ZnP and AuP–AuP) was undertaken to determine the spectra of the reduced and oxidized porphyrin units. Femtosecond transient absorption spectroscopic analysis showed that the photoexcitation of the heterometallic dyad leads to an ultrafast formation of a charge-separated state ($^{+}$ZnP–AuP$^{\bullet}$) that displays a particularly long lifetime ($\tau = 4$ ns in toluene) for such a short separation distance. The molecular orbitals of the dyad were determined by DFT quantum-chemical calculations. This theoretical study confirms that the observed intense band at $\lambda = 739$ nm corresponds to an interporphyrin charge-transfer transition from the HOMO orbital localized on the zinc porphyrin to LUMO orbitals localized on the gold porphyrin. Finally, a Hyper–Rayleigh scattering study shows that the dyad possesses a large first molecular hyperpolarizability coefficient ($\beta = 2100 \times 10^{-30}$ esu at $\lambda = 1064$ nm), thus highlighting the valuable nonlinear optical properties of this new type of push–pull porphyrin system.

Keywords: charge transfer • fluorescence • nonlinear optics • photochemistry • porphyrinoids

Introduction

The development of highly conjugated donor/π-conjugated acceptor molecular systems (D/π–A) is of particular interest due to their unusual photophysical properties that can make them particularly valuable for applications in molecular electronics,[1–3] nonlinear optics,[4–7] and solar-energy transformations.[8–11] Electronically coupled D/π–A systems are the archetypal molecules used as chromophores for quadratic hyperpolarizability and they have been found to exhibit two- or three-photon absorption cross-sections, which is also another useful property for optical limiting and fluorescence imaging.[12–20] Additionally, the intramolecular charge-transfer interactions generally found in such molecules render them promising candidates to harvest photons of the solar spectrum and to convert them into useful potentials (elec-

---

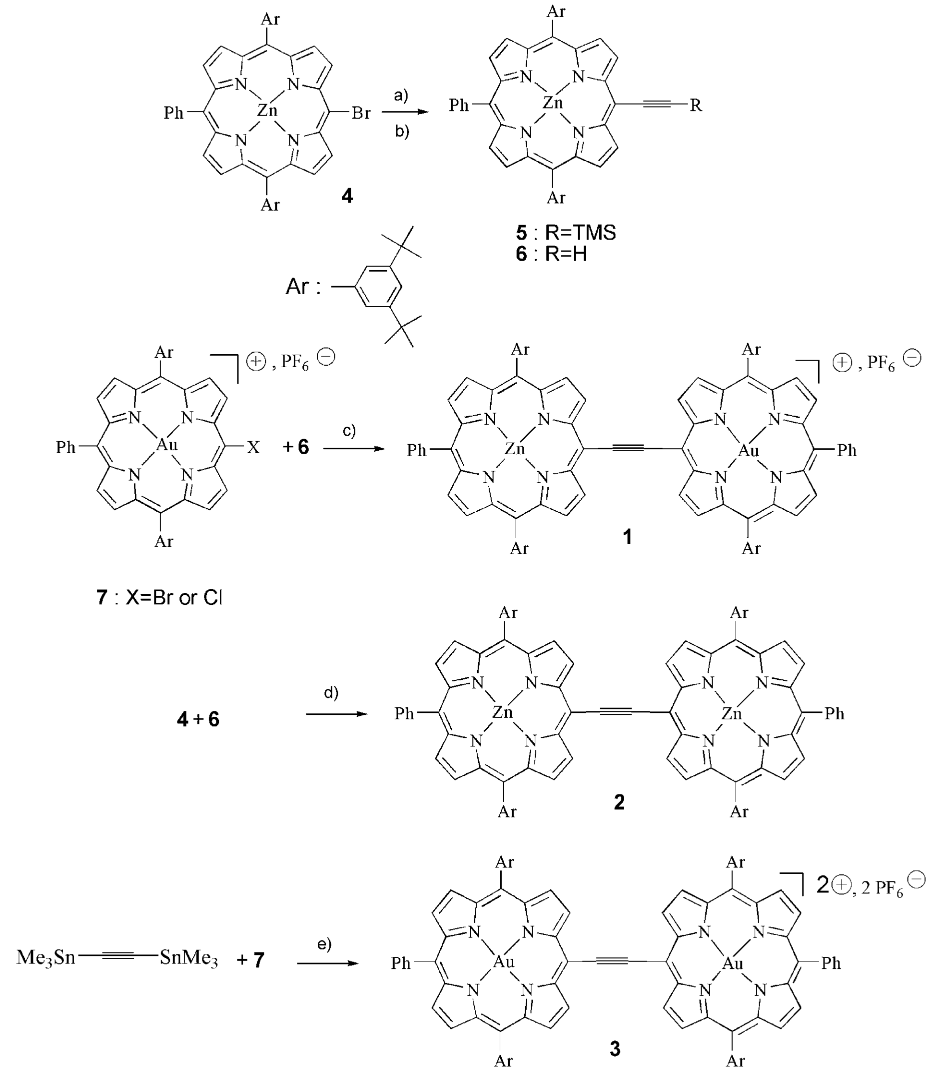
[a] Dr. J. Fortage, Dr. A. Scarpaci, Dr. L. Viau, Dr. Y. Pellegrin,
Dr. E. Blart, Dr. F. Odobel
University of Nantes, CEISAM
Chimie et Interdisciplinarité, Synthèse, Analyse, Modélisation
Faculté des Sciences et des Techniques
2, rue de la Houssinière
BP 92208, 44322 Nantes Cedex 3 (France)
E-mail: fabrice.odobel@univ-nantes.fr

[b] Dr. M. Falkenström, Prof. L. Hammarström
Department of Photochemistry and Molecular Science
The Ångström Laboratories, Uppsala University
Regementsvägen 1, 752 37 Uppsala (Sweden)
E-mail: leif.hammarstrom@fotomol.uu.se

[c] I. Asselberghs, Dr. R. Kellens, Dr. W. Libaers, Prof. K. Clays
Department of Chemistry
University of Leuven, Celestijnenlaan 200D
3001 Leuven (Belgium)
E-mail: koen.clays@fys.kuleuven.be

[d] Dr. M. P. Eng
Department of Chemistry
Imperial College London
Exhibition Road, London, SW7 2AZ (UK)
E-mail: m.eng@imperial.ac.uk

tricity or chemical fuels). For examples, push–pull organic sensitizers have been proved to be particularly efficient compounds in dye-sensitized solar cells.[21–26] Alkynyl porphyrin units have been the focus of intensive investigations by Arnold,[27–31] Anderson,[12,13,32–45] Therien,[6,7,11,46–54] Osuka,[35,36,55,56] and others.[57–65,68] Their peculiar electronic properties generally arise from the large electronic interactions due to the extensive π-electronic conjugation between triply bonded pigments. Porphyrin heterodyads that exhibit optical intramolecular electron transfer are, however, scarce in spite of the abundance of investigations for many types of applications.[66] Herein, we describe the synthesis of a new heterometallic bisporphyrin that presents a large first molecular hyperpolarizability coefficient β and a strong intramolecular charge-transfer transition in the visible spectrum that leads to a charge-separated state that lives for 4 ns in toluene at room temperature. Zinc and gold porphyrin units were chosen because they display electron-donating and -accepting properties, respectively, thus making this couple of photoactive species an interesting system for the construction of a strongly polarized chromophore that exhibits potentially valuable photochemical properties. The new heterometallic dyad **1** was thus prepared and its comprehensive photophysical properties are presented.



Scheme 1. Preparation of the electronically coupled dyads **1**–**3**. a) Trimethylsilylacetylene, CuI, $[Pd(PPh_3)_2Cl_2]$, Et_3N, THF, 30 °C (47 %); b) K_2CO_3, CH_2Cl_2, MeOH (92 %); c) **6** (1.5 equiv), **7** (1 equiv), CuI, [Pd(dppf)Cl_2], Et_3N, DMF, 45 °C (73 %); d) CuI, $[Pd_2(dba)_3]\cdot CHCl_3$, Et_3N, THF, 40 °C (41 %); e) $[Pd(PPh_3)_4]$, CuI, DMF, 110 °C (52 %). dba = dibenzylideneacetone, dppf = bis(diphenylphosphino)ferrocene, TMS = trimethylsilyl.

Results and Discussion

Synthesis: The preparation of heterometallic dyad **1** and homometallic bis-zinc **2** and bis-gold **3** reference compounds is shown in Scheme 1. The iodo trisaryl porphyrin **4** was first subjected to a Sonogashira cross-coupling reaction with trimethylsilylacetylene under the Lindsey conditions[67] to give **5**. The trimethylsilyl group was subsequently cleaved with potassium carbonate. The next step was a Sonogashira cross-coupling reaction between porphyrin **7**,[68] which is an equimolar mixture of bromo- and chloroporphyrin units, and porphyrin **6**. This coupling was catalyzed by [Pd(dppf)Cl_2] and copper iodide because good yields for the formation of other compounds containing the gold porphyrin was obtained as observed before.[68] Homometallic dimer **2** was prepared by coupling **4** with **6** under conditions reported before for similar compounds.[62] The preparation of dyad **3** gave us more difficulties than expected. We started with the demetallation of **2** to obtain the free-base porphyrin, but we failed to achieve the bis-metallation of the latter with gold. The classical conditions (i.e., $KAuCl_4$ in AcOH in presence of AcONa)[69] or milder conditions developed by Chambron et al.[70] did not afford the expected bis-gold porphyrin **3**, but only the monometallated species along with some degraded compounds. Gratifyingly, dyad **3** could be prepared by using a Stille cross-coupling reaction between the commercially available bis(trimethylstannyl)acetylene and gold porphyrin **7** under the classical conditions (i.e., $[Pd(PPh_3)_4]$ and CuI in DMF).[32]

UV/Vis absorption spectra: The UV/Vis electronic spectra of dyad **1** and the parent homometallic dimers **2** and **3** are represented in Figure 1 and the spectroscopic data gathered in Table 1. The spectra of the reference homometallic dyads **2** and **3** exhibit the usual red-shifted Q-bands located at $\lambda=695$ and 624 nm for the zinc and gold porphyrin units, respectively, and a broad split Soret band. These features are in agreement with previously described homometallic zinc porphyrin arrays linked by an ethynyl linker.[39,49,62] The clear Soret band split in the reference dyads **2** and **3** can be attributed to excitonic coupling between the two parallel strong dipolar transitions of each porphyrin along the acetylene axis with close energy levels.[46,55,71]

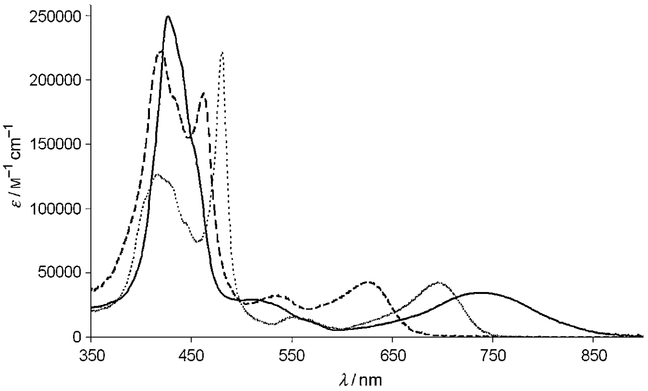


Figure 1. UV/Vis absorption spectra of dyad **1** (solid line) and the reference bis(zinc–porphyrin) **2** (dotted line) and bis(gold–porphyrin) **3** (dashed line) recorded in dichloromethane.

Table 1. Spectroscopic and electrochemical data of the dyads recorded in dichloromethane.[a]

Dyad	λ_{max} [nm] (ε [M^{-1}cm^{-1}])	$E_{1/2}$ (red) [V]	$E_{1/2}$ (Ox) [V]
1	425 (2.4×10^5), 454 (1.4×10^5), 515(2.9×10^4), 565(1.4×10^4), 739 (3.5×10^4)	−0.57, −1.07	0.81, 1.16
2	413 (1.2×10^5), 431 (1.1×10^5), 443 (8.8×10^4), 480 (2.2×10^5), 550 (1.5×10^4), 695 (4.6×10^4)		0.57, 0.77
3	417 (2.2×10^5), 461 (1.9×10^5), 533 (3.2×10^4), 624 (4.3×10^4)	−0.38, −0.54	

[a] All the potentials are referenced versus SCE.

The spectrum of the heterometallic dyad **1** differs significantly from those of homometallic dyads **2** and **3** because its spectrum is clearly not a linear combination of the spectra of **2** and **3**. The Soret band split is not observed in **1** because of the energy mismatch between the porphyrin units. Moreover, it exhibits a new absorption band at $\lambda=739$ nm, which is characteristic of neither the zinc dimer **2** nor the gold dimer **3**. We assigned this transition to an intramolecular charge-transfer band, which is the consequence of the strong through-bond electronic interactions between ZnP and AuP$^+$ through the ethynyl linkage (see below). The formation of heteroaggregates between zinc and gold porphyrin units has been reported but leads to an intermolecular transition at much higher energy (around $\lambda=600$ nm).[72] Another piece of evidence of the charge-transfer nature of the absorption band at around $\lambda=740$ nm for dyad **1** comes from the marked solvatochromism observed for this transition. The maximum absorbance of this transition is progressively red shifted when we pass from toluene ($\lambda=699$ nm; $\tilde{\nu}=14\,306$ cm^{-1}) to dichloromethane ($\lambda=739$ nm; $\tilde{\nu}=13\,532$ cm^{-1}) and to DMF ($\lambda=758$ nm; $\tilde{\nu}=13\,193$ cm^{-1}), a net total red shift of $\delta\lambda=59$ nm or $\delta\tilde{\nu}=1113$ cm^{-1}. This bathochromic shift, when the polarity of the solvent increases ("positive solvatochromism"), indicates that the excited state is stabilized by a polar solvent due to its larger dipole moment relative to the ground state. The positive solvatochromism may be surprising in view of the formally charge-shift nature of the transition, for which the band maximum would instead increase in energy with increasing solvent reorganization energy.[73,74] We propose that this apparent contradiction may be explained by the fact that the ground state of AuP$^+$ may be partially ion paired with its counteranion, at least in the less polar solvents, which would give a more charge-transfer character and thus a positive solvatochromism.

As has been carried out before for other donor/acceptor compounds that exhibit a charge-transfer transition, we estimated the magnitude of the electronic coupling V_{AB}[52,75,76] based on the Mulliken–Hush theory [Eq. (1)]:[77]

$$V_{AB} = 2.06\times10^{-2}\ (\varepsilon_{max}\nu_{max}\Delta\nu_{1/2})^{1/2}(R_{cc})^{-1} \tag{1}$$

where ε_{max} is the molar extinction coefficient (M^{-1}cm^{-1}), ν_{max} the energy (cm^{-1}) of the charge-transfer absorption, $\Delta\nu_{1/2}$ the bandwidth at half-maximum (cm^{-1}), and R_{cc} the center-to-center separation distance between the donor and acceptor (Å). From the charge-transfer transition measured in dichloromethane, the following values can be deduced: $\varepsilon_{max}=34\,700\ M^{-1}$cm^{-1}, $\nu_{max}=13\,530$ cm^{-1}, $\Delta\nu_{1/2}=2270$ cm^{-1}, and $R_{cc}=11.3$ Å[44]; thus, the electronic coupling can be calculated to be $V_{AB}=1880$ cm^{-1}. In comparison with other covalently linked ZnP/AuP$^+$ dyads,[68,78–80] this value is significantly larger and indicates that the ethynyl group promotes a very strong electronic communication between the two porphyrin units due to effective mixing of the frontier molecular orbitals of each unit.

The strong coupling suggests that the system could be close to the limit between a "localized" and "delocalized" description (classes II and III, respectively, in the mixed-valence terminology[81]), with the limit given by the condition $\lambda\approx2V_{AB}$ (λ is, herein, the reorganization energy). We note, however, that the inherent asymmetry in the redox properties of ZnP and AuP$^+$ would, even at the strong coupling limit, give a ground-state energy minimum with a character of mainly ZnP/AuP$^+$ (**1**), as opposed to a strong admixture of the biradical state. A detailed analysis of the charge-transfer parameters from the absorption band is beyond the scope of this report. We also note that the straightforward evaluation of the driving force and reorganization energy is only possible for a weakly coupled system in which $\lambda > 2V_{AB}$.

Electrochemistry and spectroelectrochemistry: The redox properties of the zinc and gold porphyrin units in dyads **1**–**3** were examined by cyclic voltammetry and differential pulse voltammetry in dichloromethane (Table 1). Interestingly, the oxidation of the two zinc porphyrin units in **2** and the reduction of the two gold porphyrin units in **3** do not coalesce in a single bielectronic wave but they appear as two stepwise processes that occur at different potentials due to the strong electronic coupling (Table 1). The two first oxidation potentials of ZnP in dyad **2** and the two first reduction potentials of AuP^+ in dyad **3** are separated by 200 and 160 mV, respectively. From these values, the comproportionation constant K_c can be calculated by using the classical equation[76,81] [Eq. (2)]:

$$\Delta E_{1/2} = 0.059 \log K_c \qquad (2)$$

The value of K_c is 2500 and 520 M^{-1} for dyads **2** and **3**, respectively, and gives an estimation of the stability of the monoradical over the corresponding diradical ($2\,ZnP\text{–}ZnP^+ \rightleftarrows ZnP^+\text{–}ZnP^+ + ZnP\text{–}ZnP$ or $2\,AuP^+\text{–}AuP^\bullet \rightleftarrows AuP^\bullet\text{–}AuP^\bullet + AuP^+\text{–}AuP^+$) and it strongly depends on the electronic coupling between the two linked units. Such large comproportionation constants mean that the electronic interaction between the two porphyrin units is relatively high and that the radical is relatively stable with respect to the dismutation reaction.

If we compare the redox potentials of the heterometallic dyad **1** with the homometallic dyads **2** and **3**, we notice that the oxidation potential of ZnP is anodically shifted by 240 mV and the reduction potential of AuP^+ is cathodically shifted by 190 mV. This outcome is certainly a consequence of the adjacent porphyrin unit in the homometallic dyad undergoing a stabilizing effect on the nearby radical (ZnP^+ or $AuP^\bullet$) with respect to the heterometallic dyad **1** and further confirms the strong electronic interactions of the two porphyrin units.

Spectroelectrochemical experiments were undertaken to elucidate the spectra of the radical cation of zinc porphyrin and the radical of gold porphyrin in dyads **1**–**3**. Note that all these electrochemical processes were reversible because reversing the potential led us to retrieve almost entirely the original spectrum. Besides, the observation of clean isosbestic points supports the transformation of one species into another without the occurrence of coupled chemical transformations (Figures 2–5). The spectrum of the radical cation of ZnP in dyad **2** upon electrolysis in situ is shown in Figure 2. The oxidation of ZnP is accompanied by a decrease in the intensity of the lower-energy Soret transition and the Q-band located at $\lambda = 696$ nm. This result confirms that the former absorption (second Soret transition at $\lambda = 480$ nm) corresponds to the excitonic coupling of the parallel transitions aligned along the ethynyl linker axis, whereas the high-energy Soret band (at $\lambda = 413$ nm) is assigned to the transition dipole perpendicular to the linkage. The new absorption at $\lambda = 890$ nm is probably an intramolecular charge-transfer transition (mixed-valence compound) with the nearby zinc porphyrin unit.

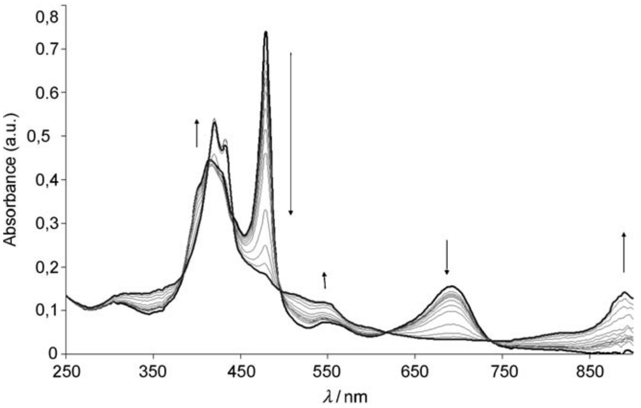


Figure 2. Transient spectra recorded upon one-electron oxidation of dyad **2** in dichloromethane. The arrows indicate the changes upon oxidation. The bold traces indicate the initial and final spectra.

The spectrum of the monoradical of the gold porphyrin unit in the homometallic dyad **3** is shown in Figure 3. The reduction of AuP^+ induces a collapse of the second Soret band (at around $\lambda = 460$ nm) and a diminution of intensity of the Q band, whereas a new absorption band grows at around $\lambda = 830$ nm. The bleaching of the Soret and Q bands is not as strong as with the oxidation of ZnP in dyad **2**. Accordingly, we suggest that the site of reduction is probably mostly metal centered with a contribution from the π-aromatic system of the porphyrin unit, as indicated by the distribution of the LUMO orbitals of this dyad (Table 2).[82] The new absorption band at $\lambda = 830$ nm is also tentatively attributed to an intramolecular charge-transfer transition as proposed above for the monooxidized bis-zinc dimer ($ZnP\text{–}ZnP^+$).

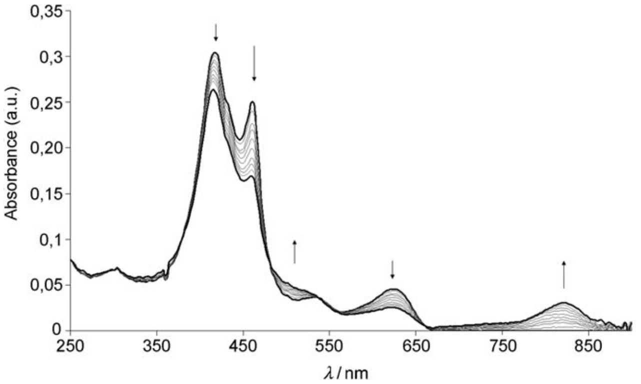
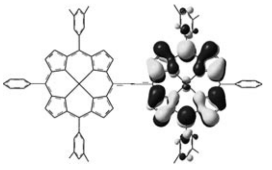
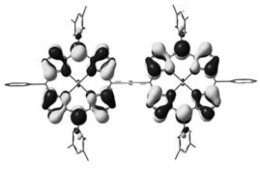
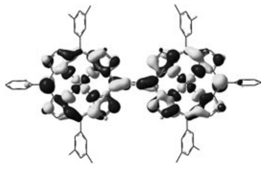
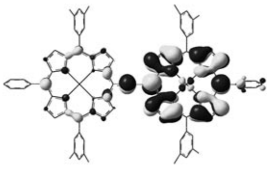
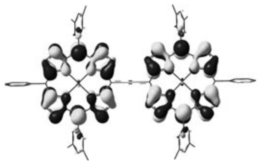
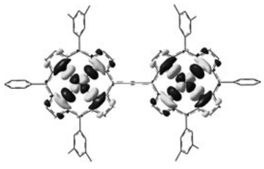
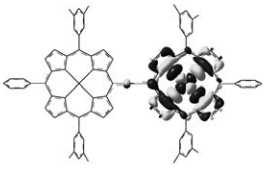
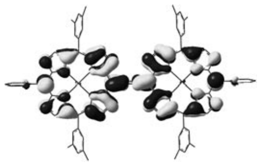
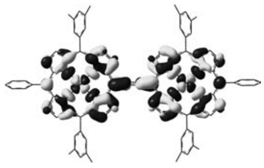
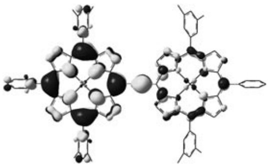
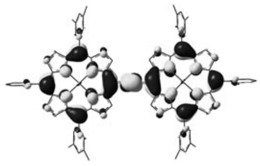
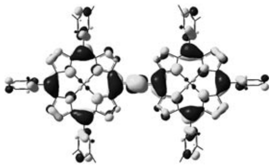


Figure 3. Transient spectra recorded upon one-electron reduction of dyad **3** in dichloromethane. The arrows indicate the changes upon oxidation. The bold traces indicate the initial and final spectra.

Table 2. Calculated Kohn–Sham (KS) orbitals of the optimized structures of dyads **1**–**3**.

KS orbitals	ZnP–AuP (**1**)	ZnP–ZnP (**2**)	AuP–AuP (**3**)
LUMO+2			
LUMO+1			
LUMO			
HOMO			

The oxidation of the zinc porphyrin in the heterometallic dyad **1** is accompanied with a bleaching of the absorption band at $\lambda = 739$ nm (Figure 4). This observation is in agreement with the attribution of the charge-transfer nature of this transition, which naturally disappears when the donor part (upon oxidation of ZnP) or acceptor part (upon reduction of AuP^+, see below) of dyad **1** is removed. The spectrum of the reduced gold porphyrin unit in dyad **1** is shown in Figure 5. As expected, the intensity of the charge-transfer band at $\lambda = 739$ nm is strongly affected by the reduction of AuP^+. Again, the Soret band is decreased in intensity during the reduction of AuP^+, but the changes are different from those observed with the oxidation of ZnP. This behavior confirms the formation of a gold(II) species rather than a π-radical anion of the porphyrin.

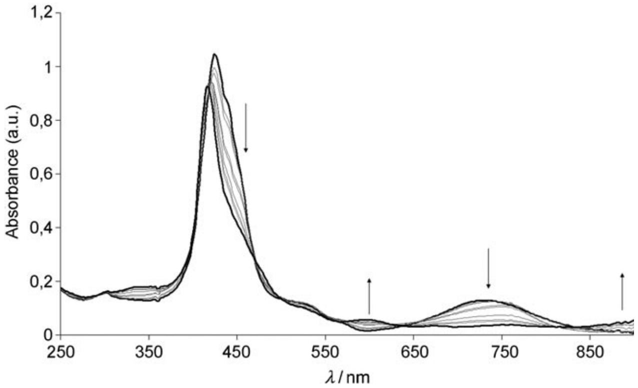


Figure 4. Transient spectra recorded upon one-electron oxidation of dyad **1** in dichloromethane. The arrows indicate the changes upon oxidation. The bold traces indicate the initial and final spectra.

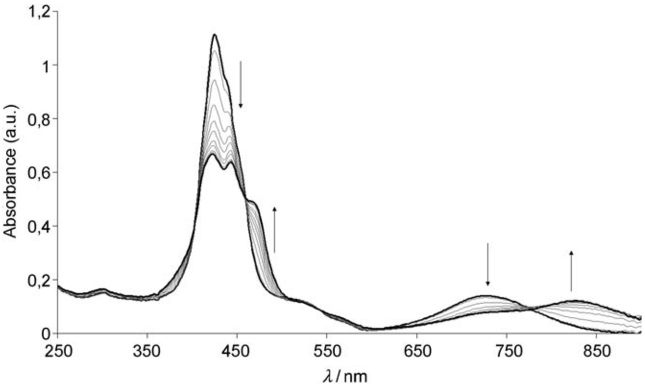


Figure 5. Transient spectra recorded upon one-electron reduction of dyad **1** in dichloromethane. The arrows indicate the changes upon reduction. The bold traces indicate the initial and final spectra.

Transient absorption spectroscopy: The photophysical properties of dyad **1** were also investigated by transient absorption spectroscopy. First, the fluorescence of the zinc porphyrin unit in dyad **1** is completely extinct. Excitation of **1** with an approximate 120-fs laser pulse in the Soret or charge-transfer band gave rise to an instant transient absorption, which we attribute to the charge-transfer state $ZnP^{\bullet+}$–$AuP^{\bullet}$ (Figure 6). In addition to bleaching of the Soret band, there are positive absorption peaks around $\lambda = 500$ and 580 nm, which correspond to changes observed upon the reduction and oxidation of **1**, respectively (Figures 4 and 5). These transient spectra recorded in DMF and dichloromethane are evolved within the instrumental time resolution (<200 fs). Some further evolution is observed in toluene on the 100-ps timescale (Figure 6).

No significant differences were observed between experiments with the Soret and charge-transfer excitation, thus indicating that the same charge-transfer state is formed within 200 fs by either photoinduced electron transfer or direct optical electron transfer. The charge-transfer state recombined completely to the ground state with single-exponential kinetics (<4% remaining signal), as illustrated by the Soret-

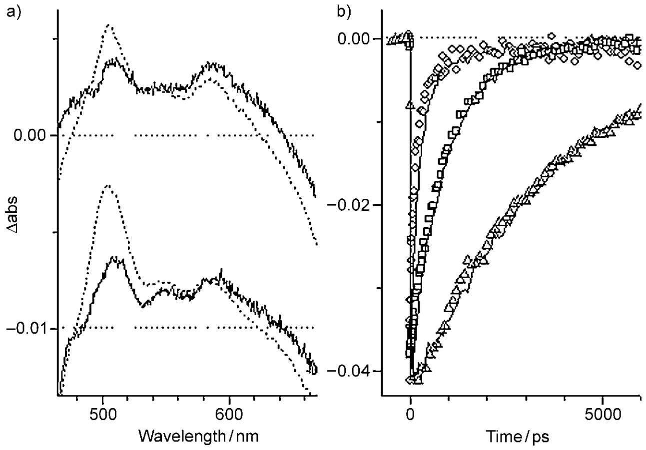


Figure 6. a) Transient absorption spectra of ZnP–AuP (**1**) recorded after 350 fs (solid lines) and 200 ps (dashed lines); excitation at $\lambda=435$ and 705 nm (upper and lower spectra, respectively). b) Transient absorption traces at $\lambda=420$ nm after excitation at $\lambda=435$ nm of ZnP–AuP (**1**) in DMF (circles), CH_2Cl_2 (squares), and toluene (triangles). The solid lines show the corresponding traces after excitation at $\lambda=705$ nm.

band bleach recovery in Figure 6 (right panel). No evidence of long-lived local porphyrin triplet states formed in the recombination process was seen. The lifetime of the charge-transfer state increased with decreasing solvent polarity from 200 ps in DMF to 1 ns in dichloromethane and 4 ns in toluene. This behavior is expected for recombination in the Marcus inverted region, in which the driving force is larger than the reorganization energy [$-\Delta G^0>\lambda$; Eq. (3)]. From the electrochemical data, the charge-transfer state should lie approximately 1.4 eV above the ground state in dichloromethane, and the value of λ in this type of system should be smaller than that. The energy of the charge-transfer state increases and the λ value decreases in low-polarity solvents, which increases the barrier to recombination and thus the charge-transfer lifetime, in agreement with our observations.

$$k_{\mathrm{ET}} = A\exp[-(\Delta G^0+\lambda)^2/4\lambda \mathrm{R}T] \qquad (3)$$

It may be surprising that this strongly coupled system leads to a similar or even longer lifetime of the charge-separated state relative to more weakly coupled hetero zinc–gold porphyrin dyads reported previously, in which the two porphyrin units were separated by a longer distance.[27,39] However, a strong coupling induces an avoided crossing between the charge-transfer and ground-state surfaces (Figure 7), and the Frank–Condon factors for the recombination becomes small. The situation is then similar to the case of nonradiative decay of a rigid fluorophore.[38]

Quantum-chemical calculations: To gain deeper insight into the nature of the excited states of **1**–**3**, a set of DFT calculations were performed. For all atoms except gold, the 6-31G(d) basis set was used.[83] For the gold centers, the LanL2DZ basis set was used,[84–86] in which the core electrons are replaced with an effective core potential (ECP) to account for relativistic effects. To decrease the computational cost, the *tert*-butyl groups were replaced by methyl groups. Each dyad was first geometry optimized with C_2 (dyad **1**) or D_2 (dyads **2** and **3**) symmetry constraints by using the B3LYP functional.[87–89] Full optimizations were verified by frequency calculations that showed no virtual frequencies. The optimizations resulted in slightly saddle-shaped structures due to the steric interactions between the porphyrin units.

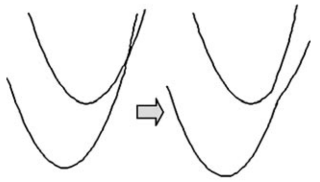


Figure 7. Schematic representation of the free-energy surfaces for the charge transfer and ground states. Left: no coupling; right: strong coupling.

The optimized structures were used for time-dependent DFT (TD-DFT) calculations of the vertical excited states by using the same functional and basis sets as for the geometry optimizations.[90–92] The solvent effects of dichlorobenzene were approximated by using the nonequilibrium version[93] of the polarizable conductor calculation model CPCM.[94,95] All the calculations were performed using the Gaussian03 software suite.[95] For simulation of the absorption spectra, each transition was approximated by a Gaussian peak with a bandwidth of 1500 cm^{-1} and the area of each peak was set to that of the calculated oscillator strength *f*.

Table 2 shows the KS orbitals of **1**–**3**. It can be seen that in the symmetric compounds (i.e., **2** and **3**) all the orbitals are equally distributed over the two porphyrin units. In these compounds, no transitions with a net charge transfer are possible from the ground state. On the other hand, there is a clear separation in **1** into orbitals localized mainly on either the zinc or gold porphyrin moieties. If the electronic coupling between the two moieties is sufficient, this arrangement should give rise to a set of transitions with a net charge transfer. The calculated properties of the lowest transition with a considerable contribution to the absorptions spectra for each compound and the experimental wavelengths for these transitions are compiled in Table 3. Figure 8 shows the simulated absorption spectra of **1**–**3**. On comparison of Figures 8 and 1, it can be seen that the calculations give a fairly good description of the experimental absorption spectra. It can, thus, be concluded from Tables 2 and 3 that the calculations support that the lowest transition observed in the absorption spectrum of dyad **1** is a charge-transfer transition. The energy of this transition is a bit underestimated, as is often the case for charge-transfer bands calculated with DFT.[96]

A recent, combined experimental and computational study of gold(III) versus zinc(II) porphyrin units showed that the LUMO of gold(III) porphyrin is metal centered.[97] The study concluded that this orbital introduces a number

Table 3. The calculated and experimental wavelengths λ and calculated oscillator strengths *f* of the lowest transitions that significantly contribute to the absorption spectra for compounds **1**–**3**.

Dyad	λ_{calcd} [nm]	λ_{exp} [nm]	*f*	Dominant configurations
ZnP–AuP (**1**)	791	739	1.2	HOMO→LUMO (15%) HOMO→LUMO+1 (73%)
ZnP–ZnP (**2**)	682	695	1.3	HOMO→LUMO (86%)
AuP–AuP (**3**)	652	625	1.1	HOMO→LUMO (48%) HOMO→LUMO+2 (39%)

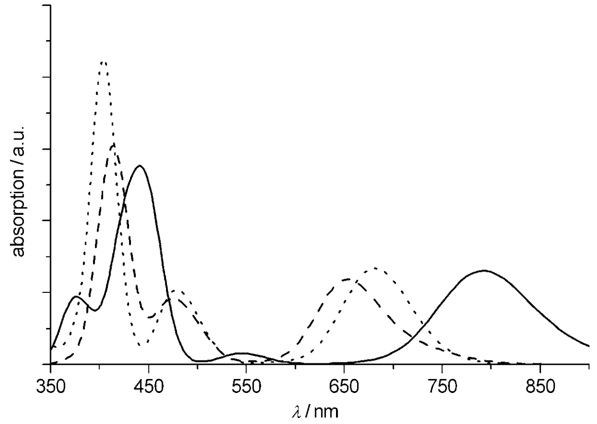


Figure 8. The simulated absorption spectra of dyads **1** (solid line), **2** (dotted line), and **3** (dashed line).

of states that does not show in the absorption spectrum but strongly dictates the excited-state dynamics. In the present case, this orbital indeed takes part in the ground-state photophysics (Tables 2 and 3). This behavior is due to symmetry breaking induced by the saddle-shaped structures and porphyrin–porphyrin interactions.

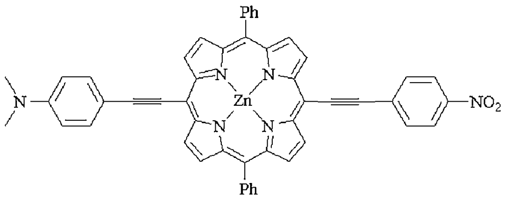
Quadratic hyperpolarizability: In addition, we studied the second-order nonlinear optical properties of dyad **1**. Because of the charged nature of this compound, Hyper–Rayleigh Scattering (HRS)[98,99] was used to assess the first hyperpolarizability (second-order nonlinear polarizability) in solution. Because the dispersion (wavelength dependence) of this molecular parameter for porphyrin-based chromophores has been previously described as unusual,[50,53] we performed HRS at λ = 800 and 1064 nm. Although the latter wavelength is provided by nanosecond pulsed lasers,[100] the former wavelength is the output of a femtosecond pulsed laser that additionally allows for discrimination between potential multiphoton fluorescence and nonlinear scattering.[101,102] We analyzed the HRS signal toward a single major dipolar hyperpolarizability tensor component *βzzz*, in which the *z* axis is the molecular charge-transfer axis. Table 4 gives the results of this analysis and the largest hyperpolarizability value from a porphyrin derivative calculated by Therien and co-workers.[50] Please note that the latter are elaborate push–pull chromophores with moieties that by themselves already exhibit nonlinear optical properties.

The first hyperpolarizability of dyad **1** is very large. The large second-order nonlinearity is a direct consequence of the strong charge-transfer interaction through this linkage. The dispersion of the first hyperpolarizability for porphyrin-based charge-transfer molecules is quite unusual.[50,53] Therefore, it is difficult to relate structure to property in a fully quantitative way at all the measurement wavelengths. The dispersion has been related to the two contributions (from the Soret and Q bands) to the nonlinear response. A much stronger effect can be expected from the one-photon resonance enhancement at λ = 800 nm caused by the charge-transfer band at λ = 740 nm in dyad **1**. This effect explains the large hyperpolarizability value at λ = 800 nm. A full quantitative analysis of the combined effect of conjugation and dispersion on the value of the first hyperpolarizability for porphyrin derivatives or dyads is beyond the present level of understanding.[50,53]

Conclusion

We have reported the preparation of a new heterometallic bisporphyrin system that displays a strong electronic coupling with an intense charge-transfer transition that yields to a relatively long-lived charge-separated state. Furthermore, this ZnP–AuP dyad exhibits interesting nonlinear optical properties that manifest by a particularly large first hyperpolarizability coefficient. The dispersion of the first hyperpolarizability value could be explained in terms of resonance enhancement caused by the spectral position of the charge-transfer band. The femtosecond transient absorption spectroscopy study revealed that light excitation of the dyad either in the Soret or charge-transfer transition leads to the immediate formation of the charge-separated state, the lifetime of which is particularly long if one refers to other zinc–gold porphyrin dyads separated by a long spacer.[68] This new electronically coupled heterometallic bisporphyrin species repre-

Table 4. Nonlinear optical data measured in dichloromethane.[a]

Compound	*βzzz* (λ = 800 nm) [10^{-30} esu]	*βzzz* (λ = 1064 nm) [10^{-30} esu]
1	3800 ± 300	2100 ± 300
		5000[a]

[a] Data is taken from ref. [6].

sents a valuable system to be used for molecular electronics, solar-energy conversion, or nonlinear optical applications.

Experimental Section

General methods: The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz or AMX 400 MHz Bruker spectrometer. Chemical shifts for the ^{1}H NMR spectra are referenced relative to residual protium in the deuterated solvent ($\delta = 7.26$ and 7.16 ppm in $CDCl_3$ and C_6D_6, respectively). The mass spectra were recorded on a EI-MS HP 5989 A spectrometer or a JMS-700 double-focusing mass spectrometer of reversed geometry equipped with an electrospray ionization (ESI) source (JEOL LTD, Akishima, Tokyo, Japan). Fast-atom bombardment mass spectrometry (FAB-MS) analyses were performed in a *meta*-nitrobenzyl-alcohol matrix (MBA) on a ZAB-HF-FAB spectrometer. MALDI-TOF analyses were performed on an Applied Biosystems Voyager DE-STR spectrometer positive linear mode with an acceleration voltage 20 kV and α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix. Electrochemical measurements were realized with an Autolab PGSTAT 302N potentiostat. A heart-shaped electrochemical cell equipped with a platinum-disk working electrode, a steel-gauze auxiliary electrode, a SCE reference electrode, and an argon inlet was used for cyclic and square-wave voltammetry. Spectroelectrochemical measurements were carried out with an optically transparent thin-layer electrochemical (OTTLE) cell fitted in the cavity of a Shimadzu UV2501-PC spectrophotometer with a platinum grid as the working electrode.

Preparative TLC analysis was performed with on Merk Kieselgel $60PF_{254}$ plates. Column chromatography was carried out with Merk 5735 Kieselgel 60F (0.040–0.063-mm mesh). Air-sensitive reactions were carried out under argon in dry solvents and glassware. Chemicals were purchased from Aldrich and used as received. Compounds zinc(II)-5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-iodoporphyrin (**4**) and gold(III)-5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-bromoporphyrin (**7**) were prepared according to previously reported methods.[68]

Hyper–Rayleigh light scattering (HRS) measurements: The experimental setup for the HRS experiments has been described in detail elsewhere.[100–102]

Zinc(II) 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-(trimethylsilylethynyl)porphyrin (5): Zinc(II)-5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-iodoporphyrin (**4**; 146 mg, 0.15 mmol), distilled Et_3N (1.5 mL), distilled THF (5 mL), copper iodide (1.5 mg, 7.67 μmol), and $[Pd(PPh_3)_2Cl_2]$ (5.4 mg, 7.67 μmol) were placed in a sealed tube, and the mixture was degassed through several freeze/thaw cycles. Trimethylsilylacetylene (65 μL, 0.46 mmol, $d = 0.69$) was added to the reaction mixture, which was stirred for 15 h at 35 °C under argon. The solvents were removed under vacuum and dichloromethane was added. The organic phase was washed with water and the aqueous phase was extracted with dichloromethane. The organic phases were collected, dried over $MgSO_4$, and concentrated to dryness. The crude mixture was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 8:2), thus affording a purple solid (66 mg, 47 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.65$ (s, 9 H; H_{TMS}), 1.58 (s, 36 H; H_{tBu}), 7.75 (m, 3 H; H_{phenyl}), 7.85 (s, 2 H; H_{para}), 8.11 (s, 4 H; H_{ortho}), 8.20 (m, 2 H; H_{phenyl}), 8.94 (dd, $^{3}J = 4.5$, $^{3}J = 16.8$ Hz, 4 H; H_{β}), 9.08 (d, $^{3}J = 4.8$ Hz, 2 H; H_{β}), 9.81 ppm (d, $^{3}J = 4.8$ Hz, 2 H; H_{β}); MALDI-TOF: *m*/*z*: calcd for $C_{59}H_{64}N_4SiZn$: 920.4 [M^+]; found: 920.4.

Zinc(II) 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-ethynylporphyrin (6): Zinc(II)-5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-(trimethylsilylethynyl)porphyrin (**5**; 92 mg, 99.9 μmol) and K_2CO_3 (138 mg, 1.0 mmol) were dissolved in a mixture of dichloromethane (1.5 mL) and methanol (3 mL). The reaction mixture was protected from light and stirred for 3.5 h at 25 °C. Dichloromethane was added and the organic phase was washed twice with water. The organic phase was dried over $MgSO_4$ and concentrated to dryness to yield a green solid (78 mg, 92 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.57$ (s, 36 H; H_{tBu}), 3.99 (s, 1 H; $H_{ethynyl}$), 7.74 (m, 3 H; H_{phenyl}), 7.85 (s, 2 H; H_{para}), 8.11 (s, 4 H; H_{ortho}), 8.20 (m, 2 H; H_{phenyl}), 8.93 (dd, $^{3}J = 4.5$, $^{3}J = 14.1$ Hz, 4 H; H_{β}), 9.06 (d, $^{3}J = 4.8$ Hz, 2 H; H_{β}), 9.69 ppm (d, $^{3}J = 4.8$ Hz, 2 H; H_{β}); MALDI-TOF: *m*/*z*: calcd for $C_{56}H_{56}N_4Zn$: 848.38 [M^+]; found: 848.58.

Dyad 1: Zinc(II) 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-ethynylporphyrin (78 mg, 0.92 mmol), an equimolar mixture of gold(III) 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-bromoporphyrin and gold(III) 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-chloroporphyrin (81 mg, 0.61 mmol), copper iodide (2.3 mg, 0.12 mmol), $[Pd(dppf)Cl_2]$ (9.2 mg, 0.12 mmol), distilled DMF (4 mL), and distilled Et_3N (0.6 mL) were placed in a sealed tube. The mixture was degassed, protected from light, and heated at 45 °C overnight. Dichloromethane was added to the crude mixture. The organic phase was washed three times, dried over $MgSO_4$, and concentrated to dryness. The solid was purified by column chromatography on silica gel (CH_2Cl_2), thus affording a dark-green solid (95 mg, 73 %). ^{1}H NMR (400 MHz, C_6D_6, 65 °C): $\delta = 1.57$ (s, 72 H; H_{tBu}), 7.49–7.54 (m, 6 H; H_{phenyl}), 8.05 (m, 2 H; H_{para}), 8.08 (m, 2 H; H_{phenyl}), 8.10 (m, 2 H; H_{para}), 8.20–8.21 (m, 2 H; H_{phenyl}), 8.35 (m, 4 H; H_{ortho}), 8.42 (m, 4 H; H_{ortho}), 8.94 (m, 2 H; H_{β}), 8.98 (m, 2 H; H_{β}), 9.12 (m, 2 H; H_{β}), 9.15 (m, 4 H; H_{β}), 9.23 (m, 2 H; H_{β}), 9.42 (m, 2 H; H_{β}), 9.49 ppm (m, 2 H; H_{β}); elemental analysis calcd (%) for $C_{110}H_{110}AuN_8ZnPF_6 \cdot 8.5\,MeOH$: C 64.0, H 6.5, N 5.0; found: C 64.5, H 6.2, N 4.5; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 425 (240 000), 454 (140 000), 515 (29 000), 565 (14 000), 739 nm (35 000 $mol^{-1}dm^{3}cm^{-1}$); HR-MALDI-TOF: *m*/*z*: calcd for $C_{110}H_{110}AuN_8Zn$: 1803.7796 [$M-PF_6$]$^+$; found: 1803.7805.

Dyad 2: Zinc(II) 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-ethynylporphyrin (27 mg, 0.030 mmol), zinc(II) 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-bromoporphyrin (31 mg, 0.034 mmol), triphenylarsine (12 mg, 0.039 mmol), $[Pd_2(dba)_3] \cdot CHCl_3$ (5 mg, 0.005 mmol), distilled THF (3.3 mL), and distilled Et_3N (0.7 mL) were placed in a sealed tube. The reaction mixture was degassed, protected from light, and heated at 40 °C for 4 h. The solvents were evaporated and the crude solid was purified by column chromatography on silica gel (petroleum ether/THF 99:1), thus affording a dark-green solid (21 mg, 41 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.57$ (s, 72 H; H_{tBu}), 7.76 (m, 2 H; H_{phenyl}), 7.77 (m, 4 H; H_{phenyl}), 7.84 (m, 4 H; H_{para}), 8.16 (m, 8 H; H_{ortho}), 8.22 (m, 4 H; H_{phenyl}), 8.90 (m, 4 H; H_{β}), 8.96 (m, 4 H; H_{β}), 9.24 (m, 4 H; H_{β}), 10.50 ppm (m, 4 H; H_{β}); elemental analysis calcd (%) for $C_{110}H_{110}N_8Zn_2 \cdot 1.5\,CHCl_3 \cdot 2.5\,THF$: C 71.7, H 6.5, N 5.5; found: C 72.1, H 6.1, N 5.2; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 413 (120 000), 431 (1150 000), 443 (88 000), 480 (220 000), 550 (15 000), 695 nm (46 000 $mol^{-1}dm^{3}cm^{-1}$); HR-MALDI-TOF: *m*/*z*: calcd for $C_{110}H_{110}N_8Zn_2$: 1670.7431 [M^+]; found: 1670.7439.

Dyad 3: Gold(III) 5,15-bis-(3,5-di-*tert*-butylphenyl)-10-phenyl-20-bromoporphyrin (60 mg, 0.051 mmol), copper iodide (3 mg, 0.017 mmol), $[Pd(PPh_3)_4]$ (10 mg, 0.0085 mmol), and distilled DMF (3 mL) were placed in a sealed tube. The reaction mixture was degassed and bis(trimethylstannyl)acetylene (9 mg, 0.025 mmol) was added. The sealed tube was protected from light and heated at 110 °C for 12 h. Diethyl ether and KPF_6 (100 mg) were added to the crude mixture. The organic phase was washed three times with water, dried over $MgSO_4$, and concentrated to dryness. The solid was purified by column chromatography on silica gel (dichloromethane/methanol 96:4), thus affording a dark-green solid (27 mg, 52 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.57$ (s, 72 H; H_{tBu}), 7.8–7.9 (m, 8 H; H_{phenyl}), 8.16 (d, $J = 1.5$ Hz, 8 H; H_{ortho}), 8.25 (m, 4 H; H_{phenyl}), 9.25 (m, $J = 5.1$ Hz, 4 H; $H_{\beta)}$, 9.31 (d, $J = 5.1$ Hz, 4 H; $H_{\beta)}$, 9.60 (d, $J = 4.8$ Hz, 4 H; $H_{\beta,}$), 10.70 ppm (d, $J = 4.8$ Hz, 4 H; $H_{\beta,}$); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 417 (220 000), 461 (190 000), 533 (32 000), 624 nm (43 000 $mol^{-1}dm^{3}cm^{-1}$); HR-MALDI-TOF: *m*/*z*: calcd for $C_{110}H_{110}Au_2N_8$: 1936.8160 [M^+]; found: 1936.8179.

Acknowledgements

I.A. is a postdoctoral research fellow of the Fund for Scientific Research Flanders (FWO). The authors acknowledge financial support from the French Ministry of Research with the ACI "jeunes chercheurs" 4057 (fellowship of J.F.) for ANR "PhotoCumElec" from the Fund for Scientific Research Flanders (G.0312.08) and the Research Council of the University of Leuven (GOA/2006/03). L.H. acknowledges support from the Swedish Foundation for Strategic Research, the K&A Wallenberg Foundation, and the Swedish Energy Agency. M.P.E. acknowledges the Knut and Alice Wallenberg Foundation for funding.

---

[1] K. Müllen, G. Wegner, *Electronic Materials: The oligomer Approach*, Wiley-VCH, Weinheim, **1998**.
[2] J. Park, N. Pasupathy Abhay, I. Goldsmith Jonas, C. Chang, Y. Yaish, R. Petta Jason, M. Rinkoski, P. Sethna James, D. Abruna Hector, L. McEuen Paul, C. Ralph Daniel, *Nature* **2002**, *417*, 722–725.
[3] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541–548.
[4] L. R. Dalton, W. H. Steier, B. H. Robinson, C. Zhang, A. Ren, S. Garner, A. Chen, T. Londergan, L. Irwin, B. Carlson, L. Fifield, G. Phelan, C. Kincaid, J. Amend, A. Jen, *J. Mater. Chem.* **1999**, *9*, 1905–1920.
[5] *Nonlinear Optical Properties of Organic Molecules and Crystals, Vol. 2*, (Eds.: D. S. Chemla, J. Zyss), Academic Press, Orlando, **1987**.
[6] S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang, M. J. Therien, *J. Am. Chem. Soc.* **1996**, *118*, 1504–1510.
[7] S. Priyadarshy, M. J. Therien, D. N. Beratan, *J. Am. Chem. Soc.* **1996**, *118*, 1497–1503.
[8] J. Jortner, M. Bixon, *Electron Transfer-From Isolated Molecules to Biomolecules*, Wiley, New York, **1999**.
[9] R. F. Kelley, M. J. Tauber, M. R. Wasielewski, *Angew. Chem.* **2006**, *118*, 8147–8150; *Angew. Chem. Int. Ed.* **2006**, *45*, 7979–7982.
[10] R. F. Kelley, M. J. Tauber, T. M. Wilson, M. R. Wasielewski, *Chem. Commun.* **2007**, 4407–4409.
[11] N. P. Redmore, I. V. Rubtsov, M. J. Therien, *J. Am. Chem. Soc.* **2003**, *125*, 8769–8778.
[12] M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, H. L. Anderson, *J. Phys. Chem. B* **2005**, *109*, 7223–7236.
[13] M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **2004**, *126*, 15352–15353.
[14] R. Kannan, G. S. He, T.-C. Lin, P. N. Prasad, R. A. Vaia and L.-S. Tan, *Chem. Mater.* **2004**, *16*, 185–194.
[15] G. S. He, P. P. Markowicz, T.-C. Lin, P. N. Prasad, *Nature* **2002**, *415*, 767–770.
[16] M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, C. Xu, *Science* **1998**, *281*.
[17] T. Ishi-i, Y. Taguri, S.-i. Kato, M. Shigeiwa, H. Gorohmaru, S. Maeda, S. Mataka, *J. Mater. Chem.* **2007**, *17*, 3341–3346.
[18] M.-C. Yoon, S. B. Noh, A. Tsuda, Y. Nakamura, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2007**, *129*, 10080–10081.
[19] O. Rubio-Pons, Y. Luo, H. Agren, *J. Chem. Phys.* **2006**, *124*, 094310/094311–094310/094315.
[20] M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **2004**, *126*, 15352–15353.
[21] H. Choi, C. Baik, S. O. Kang, J. Ko, M.-S. Kang, M. K. Nazeeruddin, M. Graetzel, *Angew. Chem.* **2008**, *120*, 333–336; *Angew. Chem. Int. Ed.* **2008**, *47*, 327–330.
[22] S. Hwang, J. H. Lee, C. Park, H. Lee, C. Kim, C. Park, M.-H. Lee, W. Lee, J. Park, K. Kim, N.-G. Park, C. Kim, *Chem. Commun.* **2007**, 4887–4889.
[23] I. Jung, J. K. Lee, K. H. Song, K. Song, S. O. Kang, J. Ko, *J. Org. Chem.* **2007**, *72*, 3652–3658.
[24] M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen, Z. Li, *J. Phys. Chem. C* **2007**, *111*, 4465–4472.
[25] N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, *J. Am. Chem. Soc.* **2006**, *128*, 14256–14257.
[26] S. Kim, J. K. Lee, S. O. Kang, J. Ko, J. H. Yum, S. Fantacci, F. De Angelis, D. Di Censo, M. K. Nazeeruddin, M. Graetzel, *J. Am. Chem. Soc.* **2006**, *128*, 16701–16707.
[27] R. Stranger, J. E. McGrady, D. P. Arnold, I. Lane, G. A. Heath, *Inorg. Chem.* **1996**, *35*, 7791–7797.
[28] D. P. Arnold, G. A. Heath, D. A. James, *J. Porphyrins Phthalocyanines* **1999**, *3*, 5–31.
[29] D. P. Arnold, G. A. Heath, *J. Am. Chem. Soc.* **1993**, *115*, 12197–12198.
[30] D. P. Arnold, L. J. Nitschinsk, *Tetrahedron Lett.* **1993**, *34*, 693–696.
[31] D. P. Arnold, R. D. Hartnell, *Tetrahedron* **2001**, *57*, 1335–1345.
[32] M. J. Frampton, H. Akdas, A. R. Cowley, J. E. Rogers, J. E. Slagle, P. A. Fleitz, M. Drobizhev, A. Rebane, H. L. Anderson, *Org. Lett.* **2005**, *7*, 5365–5368.
[33] I. M. Blake, A. Krivokapic, M. Katterle, H. L. Anderson, *Chem. Commun.* **2002**, 1662–1663.
[34] T. E. O. Screen, I. M. Blake, L. H. Rees, W. Clegg, S. J. Borwick, H. L. Anderson, *J. Chem. Soc. Perkin Trans. 1* **2002**, 320–329.
[35] J. J. Piet, P. N. Taylor, B. R. Wegewijs, H. L. Anderson, A. Osuka, J. M. Warman, *J. Phys. Chem. B* **2001**, *105*, 97–104.
[36] J. J. Piet, P. N. Taylor, H. L. Anderson, A. Osuka, J. M. Warman, *J. Am. Chem. Soc.* **2000**, *122*, 1749–1757.
[37] S. M. Kuebler, R. G. Denning, H. L. Anderson, *J. Am. Chem. Soc.* **2000**, *122*, 339–347.
[38] H. L. Anderson, *Angew. Chem.* **2000**, *112*, 2552–2554; *Angew. Chem. Int. Ed.* **2000**, *39*, 2451–2453.
[39] I. M. Blake, L. H. Rees, T. D. W. Claridge, H. L. Anderson, *Angew. Chem.* **2000**, *112*, 1888–1891; *Angew. Chem. Int. Ed.* **2000**, *39*, 1818–1821.
[40] J. R. G. Thorne, S. M. Kuebler, R. G. Denning, I. M. Blake, P. N. Taylor, H. L. Anderson, *Chem. Phys.* **1999**, *248*, 181–193.
[41] H. L. Anderson, *Chem. Commun.* **1999**, 2323–2330.
[42] H. L. Anderson, A. P. Wylie, K. Prout, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1607–1611.
[43] I. M. Blake, H. L. Anderson, D. Beljonne, J.-L. Bredas, W. Clegg, *J. Am. Chem. Soc.* **1998**, *120*, 10764–10765.
[44] P. N. Taylor, J. Huuskonen, R. T. Aplin, H. L. Anderson, J. Huuskonen, G. Rumbles, E. Williams, *Chem. Commun.* **1998**, 909–910.
[45] H. L. Anderson, *Tetrahedron Lett.* **1992**, *33*, 1101–1104.
[46] V. S. Lin, S. G. DiMagno, M. J. Therien, *Science* **1994**, *264*, 1105–1111.
[47] V. S. Y. Lin, M. J. Therien, *Chem. Eur. J.* **1996**, *1*, 645–651.
[48] S. M. LeCours, S. G. DiMagno, M. J. Therien, *J. Am. Chem. Soc.* **1996**, *118*, 11854–11864.
[49] R. Shediac, M. H. B. Gray, H. T. Uyeda, R. C. Johnson, J. T. Hupp, P. J. Angiolillo, M. J. Therien, *J. Am. Chem. Soc.* **2000**, *122*, 7017–7033.
[50] H. T. Uyeda, Y. Zhao, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, M. J. Therien, *J. Am. Chem. Soc.* **2002**, *124*, 13806–13813.
[51] K. Susumu, M. J. Therien, *J. Am. Chem. Soc.* **2002**, *124*, 8550–8552.
[52] I. V. Rubtsov, Y. K. Kang, N. P. Redmore, R. M. Allen, J. Zheng, D. N. Beratan, M. J. Therien, *J. Am. Chem. Soc.* **2004**, *126*, 5022–5023.
[53] T.-G. Zhang, Y. Zhao, I. Asselberghs, A. Persoons, K. Clays, M. J. Therien, *J. Am. Chem. Soc.* **2005**, *127*, 9710–9720.
[54] T. V. Duncan, K. Susumu, L. E. Sinks, M. J. Therien, *J. Am. Chem. Soc.* **2006**, *128*, 9000–9001.
[55] Y. H. Kim, D. H. Jeong, D. Kim, S. C. Jeoung, H. S. Cho, S. K. Kim, N. Aratani, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 76–86.
[56] A. Osuka, H. Shimidzu, *Angew. Chem.* **1997**, *109*, 93–95; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 135–137.
[57] D. A. Shultz, K. P. Gwaltney, H. Lee, *J. Org. Chem.* **1998**, *63*, 769–774.
[58] D. A. Shultz, K. P. Gwaltney, H. Lee, *J. Org. Chem.* **1998**, *63*, 4034–4038.
[59] D. A. Shultz, H. Lee, K. P. Gwaltney, *J. Org. Chem.* **1998**, *63*, 7584–7585.
[60] J. J. Gosper, M. Ali, *J. Chem. Soc. Chem. Commun.* **1994**, 1707–1708.

[61] H. Higuchi, T. Maeda, K. Miyabayashi, M. Miyake, K. Yamamoto, *Tetrahedron Lett.* **2002**, *43*, 3097–3100.
[62] T.-H. Huang, Y.-J. Chen, S.-S. Lo, W.-N. Yen, C.-L. Mai, M.-C. Kuo, C.-Y. Yeh, *Dalton Trans.* **2006**, 2207–2213.
[63] M. Yeung, A. C. H. Ng, M. G. B. Drew, E. Vorpagel, E. M. Breitung, R. J. McMahon, D. K. P. Ng, *J. Org. Chem.* **1998**, *63*, 7143–7150.
[64] H. Yamada, K. Kushibe, T. Okujima, H. Uno, N. Ono, *Chem. Commun.* **2006**, 383–385.
[65] J. Wytko, V. Berl, M. McLaughlin, R. R. Tykwinski, M. Schreiber, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1998**, *81*, 1964–1977.
[66] K. M. Kadish, K. M. Smith, R. Guilard, *The Porphyrin Handbook*, **1999**, p. .
[67] R. W. Wagner, T. E. Johnson, F. Li, J. S. Lindsey, *J. Org. Chem.* **1995**, *60*, 5266–5273.
[68] a) J. Fortage, J. Boixel, E. Blart, L. Hammarström, H.-C. Becker, F. Odobel, *Chem. Eur. J.* **2008**, *14*, 3467–3480; b) J. Fortage, J. Boixel, E. Blart, L. Hammarström, H.-C. Becker, F. Odobel, *Inorg. Chem.* **2009** *48*, 518–526.
[69] A. Antipas, D. Dolphin, M. Gouterman, E. C. Johnson, *J. Am. Chem. Soc.* **1978**, *100*, 7705–7709.
[70] J.-C. Chambron, V. Heitz, J.-P. Sauvage, *New J. Chem.* **1997**, *21*, 237–240.
[71] Y. Kobuke, *Eur. J. Inorg. Chem.* **2006**, 2333–2351.
[72] H. Segawa, C. Takehara, K. Honda, T. Shimidzu, T. Asahi, N. Mataga, *J. Phys. Chem.* **1992**, *96*, 503–506.
[73] P. Chen, T. J. Meyer, *Chem. Rev.* **1998**, *98*, 1439–1478.
[74] N. Sutin, *Prog. Inorg. Chem.* **1983**, *30*, 441–498.
[75] D. M. Guldi, A. Gouloumis, P. Vazquez, T. Torres, *Chem. Commun.* **2002**, 2056–2057.
[76] J. E. Sutton, P. M. Sutton, H. Taube, *Inorg. Chem.* **1979**, *18*, 1017–1021.
[77] P. F. Barbara, T. J. Meyer, M. A. Ratner, *J. Phys. Chem.* **1996**, *100*, 13148–13168.
[78] J. C. Chambron, A. Harriman, V. Heitz, J. P. Sauvage, *J. Am. Chem. Soc.* **1993**, *115*, 7419–7425.
[79] M. Andersson, M. Linke, J.-C. Chambron, J. Davidsson, V. Heitz, L. Hammarström, J.-P. Sauvage, *J. Am. Chem. Soc.* **2002**, *124*, 4347–4362.
[80] K. Pettersson, J. Wiberg, T. Ljungdahl, J. Martensson, B. Albinsson, *J. Phys. Chem. A* **2006**, *110*, 319–326.
[81] D. E. Richardson, H. Taube, *Inorg. Chem.* **1981**, *20*, 1278–1285.
[82] K. M. Kadish, E. Wenbo, Z. P. Ou, J. G. Shao, P. J. Sintic, K. Ohkubo, S. Fukuzumi, M. J. Crossley, *Chem. Commun.* **2002**, 356–357.
[83] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724–728.
[84] P. J. Hay, R. W. Willard, *J. Chem. Phys.* **1985**, *82*, 270–283.
[85] R. W. Willard, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284–298.
[86] P. J. Hay, R. W. Willard, *J. Chem. Phys.* **1985**, *82*, 299–310.
[87] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[88] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[89] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.
[90] R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454.
[91] E. C. Mark, J. Christine, C. C. Kim, R. S. Dennis, *J. Chem. Phys.* **1998**, *108*, 4439–4449.
[92] R. E. Stratmann, E. S. Gustavo, J. F. Michael, *J. Chem. Phys.* **1998**, *109*, 8218–8224.
[93] M. Cossi, V. Barone, *J. Chem. Phys.* **2001**, *115*, 4708–4717.
[94] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001.
[95] Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. Vreven, T., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Lyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
[96] A. Dreuw, J. L. Weisman, M. Head-Gordon, *J. Chem. Phys.* **2003**, *119*, 2943.
[97] M. P. Eng, T. Ljungdahl, J. Andréasson, J. Mårtensson, B. Albinsson, *J. Phys. Chem. A* **2005**, *109*, 1776–1784.
[98] K. Clays, A. Persoons, *Phys. Rev. Lett.* **1991**, *66*, 2980–2983.
[99] K. Clays, A. Persoons, L. De Maeyer, *Adv. Chem. Phys.* **1993**, *85*, 455–498.
[100] K. Clays, A. Persoons, *Rev. Sci. Instrum.* **1992**, *63*, 3285–3289.
[101] G. Olbrechts, R. Strobbe, K. Clays, A. Persoons, *Rev. Sci. Instrum.* **1998**, *69*, 2233–2241.
[102] K. Clays, G. Olbrechts, T. Munters, A. Persoons, O.-K. Kim, L.-S. Choi, *Chem. Phys. Lett.* **1998**, *293*, 337–342.

Received: January 30, 2009