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# Flavin Core as Electron Acceptor Component in a Zinc(II)-Phthalocyanine-Based Dyad

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A zinc(II)-phthalocyanine-flavin dyad has been synthesized by Heck-type cross-coupling between a flavin that bears a *p*-iodophenyl group and a phthalocyanine functionalized with a vinyl moiety. Electrochemical experiments reveal that no significant interaction occurs at the ground state between the two electroactive subunits. However, the occurrence of a photoinduced electron transfer in this donor–acceptor conjugate is observed in transient absorption experiments. Charge-separation (i.e., $4.0 \times 10^{11}$ s$^{-1}$) and charge-recombination dynamics in benzonitrile ($2.2 \times 10^{10}$ s$^{-1}$) reveal a remarkable stabilization of the radical ion pair in this solvent.

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## Introduction

The induction and control of many important biological processes rely on light signals that are collected and mediated by chromophores, which are known to subsequently trigger cascades of electron and/or energy transfer events. Thus, photoinduced electron transfer is a basic process in biology, but also in chemistry and materials science. For chemists, it has become a fascinating challenge to design and tailor synthetic electron-donor–acceptor systems[1] that contain a variety of electron-donor and electron-acceptor moieties,[2] separated by a proper spacer, to gain control over light energy conversion processes.

Phthalocyanines (Pcs)[3] are synthetic tetrabenzotetraazaporphyrins that have drawn considerable attention as molecular materials. It is mainly their outstanding electronic and optical properties that drive this development.[4] In particular, they are perfectly suited as integrated components for light energy conversion systems; they exhibit very high extinction coefficients around 700 nm – a range where the maximum of the solar photon flux occurs – for efficient photon harvesting and rich redox chemistry. For this reason, Pcs have been used as chromophores in plastic solar cells[5] and for the sensitization of nanocrystalline, mesoporous $TiO_2$ films.[6] With the goal of understanding the basic processes of photoinduced electron and energy transfer in photoactive Pc-containing ensembles and potential applications in molecular photovoltaics, different electroactive systems – which include porphyrin,[7] fullerene ($C_{60}$),[8] anthraquinone,[9] perylendiimide,[10] subphthalocyanine,[11] single-walled nanotubes,[12] and ruthenium-trisbipyridine complexes[13] – have been combined with Pcs. In most of the resulting electron-donor–acceptor ensembles, Pcs perform as donor moieties, especially when $Zn^{II}$ is complexed in the central cavity of the macrocycle.

Natural chromophores that contain isoalloxazine rings are called flavins, and flavin-containing proteins are known as flavoproteins,[14] which play an essential role in oxidoreduction reactions,[15] and as blue-light sensitive photoreceptors.[16] Flavins bear electron-accepting character and, for that reason, electron-donor–acceptor ensembles based on isoalloxazine dyes covalently linked to electron-donor dyes have emerged as artificial model systems for their biological counterparts. To this end, artificial systems that contain phenothiazine-flavin as a donor–acceptor redox unit and pyrene as antenna have been constructed to model photoinduced energy and electron transfer processes of natural blue-light photoreceptors.[17] Porphyrin-flavin dyads have also been prepared and examined in the context of determining energy- and electron-transfer processes between the two moieties.[18]

With the goal of testing new donor–acceptor models, we aimed to synthesize a ZnPc-flavin dyad **1** (Scheme 1), where the two electroactive subunits were covalently linked through a styryl spacer that connected nitrogen-10 of flavin and the periphery of the Pc, and to explore the electrochemical and photoinduced electron-transfer properties in this novel system.

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## Results and Discussion

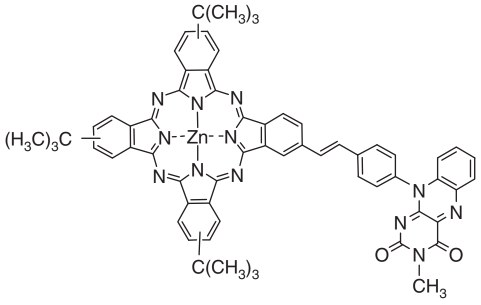
The methodology for the preparation of N(10)-substituted flavins has been previously described by Yoneda et al.[19] In particular, we aimed to prepare flavin **4** (Scheme 2), which bears a *p*-iodophenyl group at position 10, as a precursor for a subsequent Heck-type cross-coupling with phthalocyanine **5** functionalized with a vinyl moiety and three solubilizing *tert*-butyl groups at the periphery of the macrocycle (Scheme 3). The reaction between 6-chloro-3-methyluracile (**2**)[20] and commercially available 4-iodoaniline in a mixture of diethylaniline and acetic acid afforded 6-(4-iodoanilinyl)-3-methyluracile (**3**). The condensation of the latter with nitrosobenzene in a $Ac_2O$/AcOH mixture led to flavin **4** as a yellow solid in 38% overall yield.

The synthesis of ZnPc-flavin **1** was carried out by a cross-coupling Heck-type reaction between the unsymmetrically substituted $Zn^{II}$-vinylphthalocyanine **5**[21] and flavin **4** using Jeffery's protocol (see Scheme 3).[22] The product was isolated from the reaction mixture by column chromatography as a green fluorescent solid in 52% yield. The $^1H$ NMR spectrum of ZnPc-flavin **1** shows broadened aromatic and vinylic signals owing to the presence of several positional isomers, although it is easy to assign the flavin's methyl group (3.5 ppm) and *tert*-butyl groups (1.9–1.6 ppm). The UV-vis spectrum of ZnPc-flavin **1** (Fig. 1) displays both the Soret band at 350 nm and a slightly split Q-band at around 692 nm, which corresponds to the Pc core. The Q-band is shifted by 13 nm relative to that seen in the vinylphthalocyanine **5** (Fig. 1). The spectrum of ZnPc-flavin **1** also shows a continuous band between 400 and 500 nm as part of the flavin subunit.

### *Electrochemical Measurements*

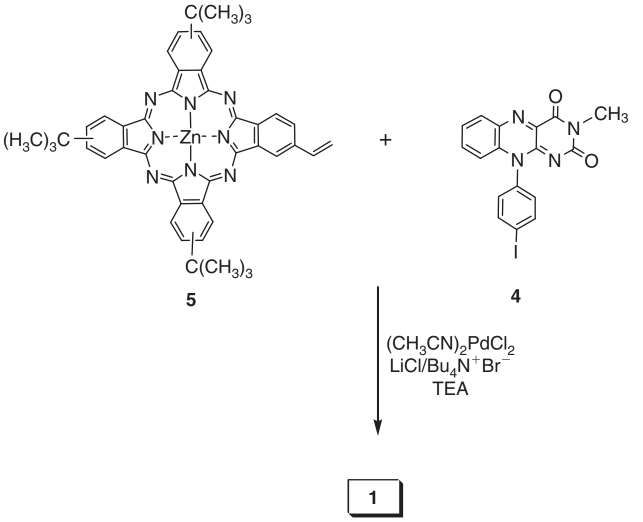
The electrochemical behaviour of Pc-flavin dyad **1** and reference compounds **4** and **5** were studied using cyclic voltammetry (CV) and the results are summarized in Fig. 2. The potential data are collected in Table 1.

The CV shows that flavin **4** is electrochemically active in the cathodic sweep direction between 0 and −2.0 V. It exhibits two one-electron cathodic peaks, one of them reversible ($\Delta E_p^1 = 63$ mV) ($\nu = 20$–$600$ mV s$^{-1}$) at around −1.02 V and another one chemically irreversible at around −1.55 V (Fig. 2). Vinylphthalocyanine **5** is electrochemically active in both anodic and cathodic sweep directions between +1.2 and −2.0 V. On the cathodic scan (Fig. 2) compound **5** exhibits three one-electron quasi-irreversible cathodic peaks ($\Delta E_p^1 = 55$ mV, $\Delta E_p^2 = 120$ mV, and $\Delta E_p^3 = 102$ mV) ($\nu = 20$–$600$ mV s$^{-1}$) at around −1.04, −1.27, and −1.49 V, respectively. In the anodic scan, this phthalocyanine shows a two-electron oxidation peak at around 0.59 V.



**1**

**Scheme 1.**



**Scheme 3.** Synthesis of ZnPc-flavin **1**.

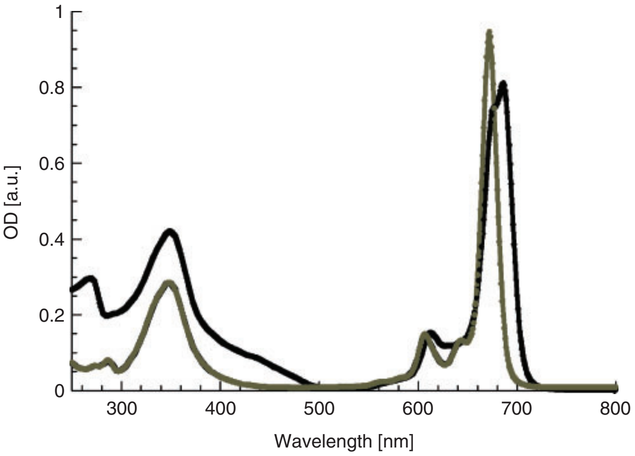
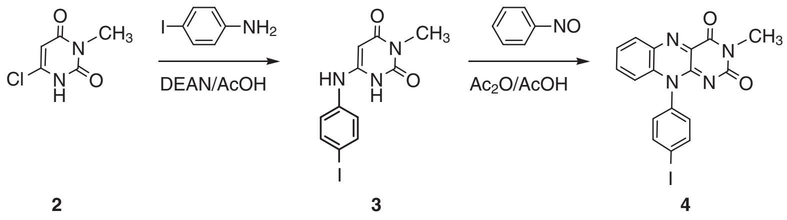


**Fig. 1.** Absorption spectra of vinylphthalocyanine **5** (dashed line) and ZnPc-flavin **1** (black line) in THF.



**Scheme 2.** Synthesis of flavin **4**.

The CV of dyad **1** (Fig. 2) shows three reduction processes on the cathodic scan sweep ($\Delta E_p^1 = 63$ mV, $\Delta E_p^2 = 70$ mV, and $\Delta E_p^3 = 95$ mV) ($\nu = 100$–$600\,\mathrm{mV\,s^{-1}}$) at around −1.03, −1.29, and −1.59 V, which can be assigned as follows: the first one probably corresponds to the overlapped first reduction waves of both Pc and flavin subunits, the second peak to the second Pc-based reduction wave, and the third one to the overlap of the third Pc-based reduction wave with the second flavin reduction peak. On the anodic scan one can observe the unresolved Pc-based two-electron oxidation process at around 0.58 V.

The results presented above indicate that there are very small potential differences observed for the subunits of dyad **1** when compared with those observed for the model compounds **4** and **5**, which indicates a negligible interaction between the moieties in the ground state.

### *Photophysical Experiments*

Insight into electron-donor–acceptor interactions between the $\mathrm{Zn^{II}}$-Pc and the flavin subunits came from fluorescence measurements. In light of the different contributions in the absorption spectrum (i.e., flavin component in the blue and ZnPc component unit in the red, Fig. 1) we decided to focus on the exclusive excitation in the 600 to 700 nm range, where merely the ZnPc component has been shown to absorb. In the steady state measurements with reference Pc (ZnPc),* we recorded a fluorescence spectrum that exhibits a strong *0–0 transition at 678 nm followed by vibrational fine structure (i.e., *0–1, *0–2, etc.) at lower energies. Important is a small Stokes shift, that is, the energetic difference between the long-wavelength absorption and short-wavelength fluorescence of only 5 nm, which speaks for the structural rigidity of the Pc. The quantum yields for the radiative pathway are 0.3 with an underlying lifetime – measured in time-resolved measurements – of 3.9 ns. In relation to the reference ZnPc, the corresponding values for ZnPc-flavin **1** are changed (Fig. 3). First, the *0–0 transition is shifted to the red, which is similar to what has been concluded for the ground state absorption. Second, the quantum yields are much lower with values, for example, 0.03 in tetrahydrofuran (THF) and 0.009 in benzonitrile. From this we derive quenching factors of 10 and 37 in THF and benzonitrile, respectively. Finally, the fluorescence lifetimes are as short as 0.254 ns in THF. In particular, the solvent dependence of the excited state deactivation points to a charge transfer that evolves between the photoexcited ZnPc chromophore and the electron accepting flavin. From electrochemical experiments we estimate that the energy of this radical ion pair state is 1.61 eV, which is 0.18 eV lower than that of the ZnPc singlet excited state.

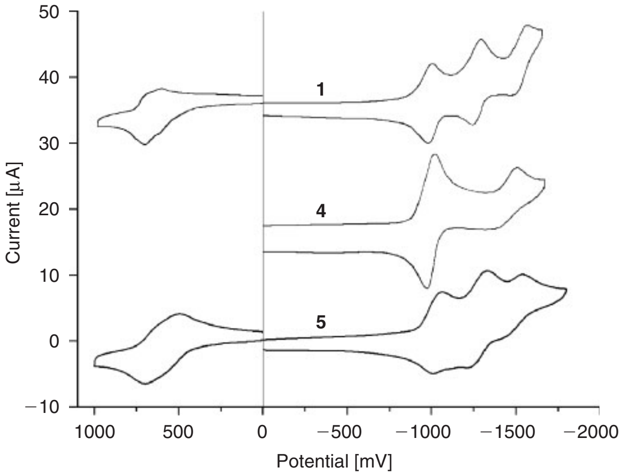


**Fig. 2.** Cyclic voltammograms (sweep rate $0.1\,\mathrm{V\,s^{-1}}$) for **1**, **4**, and **5** in *o*-DCB that contained $n$-$\mathrm{Bu_4NPF_6}$ at room temperature.

**Table 1. Electrochemical data [V *v.* Ag/AgCl] for the redox processes of compounds 1, 4, and 5 obtained by CV in *o*-DCB solutions (0.1 M *n*-Bu$_4$NPF$_6$) at room temperature under identical experimental conditions**

| Compound | $E^1_{\mathrm{red}}$ [A] | $E^2_{\mathrm{red}}$ | $E^3_{\mathrm{red}}$ [B] | $E_{\mathrm{ox}}$ |
|---|---|---|---|---|
| **1** | −1.03 | −1.29 | −1.59 | 0.58 |
| **4** | −1.02 | −1.55[C] | | |
| **5** | −1.04 | −1.27 | −1.49 | 0.59 |

[A] First Pc and flavin potentials are overlapped.
[B] Third Pc and second flavin potentials are overlapped.
[C] Chemically irreversible.

To gather spectroscopic support for this charge-transfer postulate we turned to time-resolved differential absorption measurements following photoexcitation at 670 nm. However, let's first turn to the reference ZnPc, whose transients are collected in Fig. 4. Here, we see the instantaneous formation (i.e., >1 ps) of the ZnPc singlet excited state. Spectroscopic attributes of this transient are minima around 608 and 670 nm, which are a good reflection of the ground state bleaching, and maxima at 490 nm and in the range between 750 and 1000 nm. This transient was found to be metastable, since it decays rather slowly (i.e., $3.2 \times 10^8\,\mathrm{s^{-1}}$, Fig. 4) by intersystem crossing to the energetically lower lying triplet excited state. A quantum yield of ~70% has been derived for the triplet formation. The latter is oxygen sensitive to singlet oxygen with nearly diffusion-controlled rate constants (i.e., $10^9\,\mathrm{M^{-1}\,s^{-1}}$). In the absence of molecular oxygen the lifetime of the $\mathrm{Zn^{II}}$-Pc triplet excited state is ~100 ms.

Quite different are the changes upon photoexciting ZnPc-flavin **1**. Although initially the singlet–singlet features of the

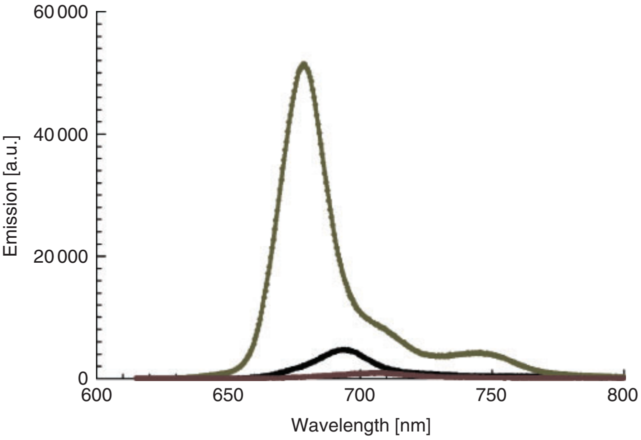


**Fig. 3.** Fluorescence spectra of reference ZnPc (dashed line) and ZnPc-flavin **1** in THF (black line) and benzonitrile (dotted line) upon 608 nm photoexcitation.

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* ZnPc (reference Pc, Zinc$^{\mathrm{II}}$ 2,9,16,23-tetra-*tert*-butylphthalocyanine) is commercially available and has an absorption spectrum in THF, which resembles that of vinylphthalocyanine **5**.

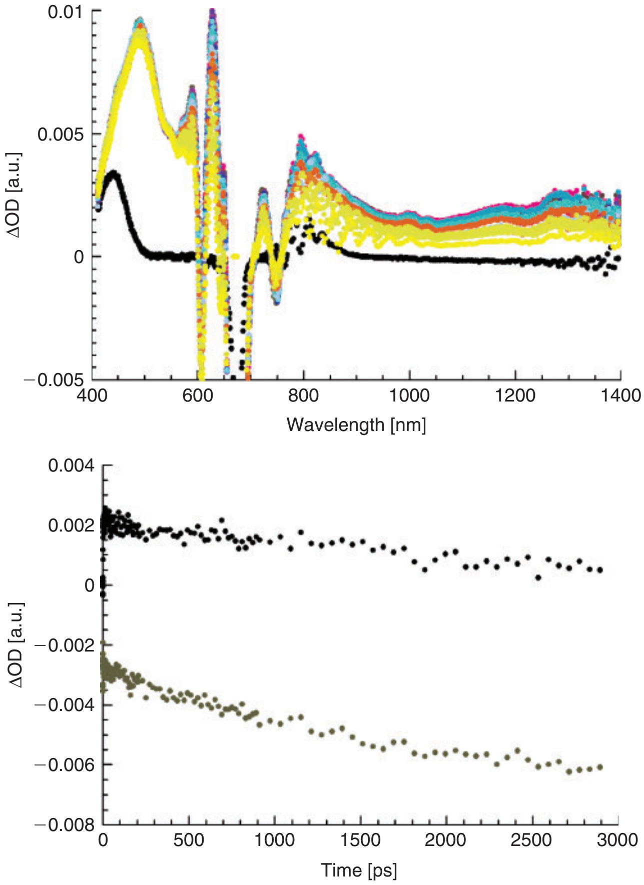

**Fig. 4.** Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (670 nm) of reference ZnPc in argon-saturated benzonitrile with several time delays at room temperature. Lower part: time–absorption profiles of the spectra shown above at 620 (i.e., open cicles) and 740 nm (i.e., closed circles), monitoring the intersystem crossing.

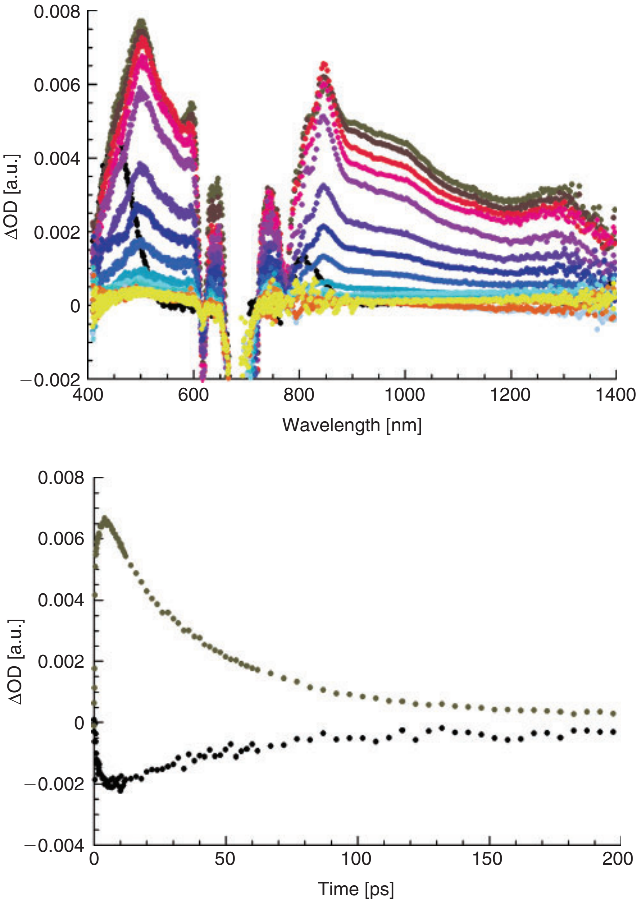

**Fig. 5.** Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (670 nm) of ZnPc-flavin **1** in argon-saturated benzonitrile with several time delays at room temperature. Lower part: time–absorption profiles of the spectra shown above at 618 nm (i.e., closed circles) and 845 nm (i.e., open cicles), monitoring the charge separation and charge recombination.

ZnPc component are discernable, these transform rather rapidly (i.e., $4.0 \times 10^{11}\ \mathrm{s}^{-1}$) in benzonitrile to a new photoproduct. Figure 5 underlines this transformation spectroscopically and kinetically. An important spectroscopic feature of the new photoproduct, which assists in assigning it to a radical ion pair state, is a maximum around 845 nm. Numerous electrochemical, radiolytic, and photolytic investigations have demonstrated that this is a clear fingerprint of the one electron oxidized radical cation of the ZnPc core.[6] Also the transient maximum in the visible region (i.e., 505 nm) is part of this radical cation spectrum. To gather evidence for the one electron reduction of flavin is rendered more difficult. In this context, a pulse radiolytic study, which focussed on the reduction of flavin with hydrated electrons, is particularly helpful. In this work[23] it has been shown that $(\text{flavin})^{\bullet -}$ gives rise to a maximum at 370 nm, which is, however, outside of the spectroscopic window of our experimental set-up. This maximum is followed by a somewhat weaker shoulder/maximum at 440 nm. A close inspection of the 400 to 500 nm range helps to identify features that are reminiscent of the pulse radiolytic data: a shoulder/maximum at 440 nm. In turn, the listed spectroscopic signatures corroborate the formation of the $(\text{ZnPc})^{\bullet +}$–$(\text{flavin})^{\bullet -}$ radical ion pair state. Figure 5 also demonstrates that the $(\text{ZnPc})^{\bullet +}$–$(\text{flavin})^{\bullet -}$ radical ion pair state decays on a time scale of several tens of picoseconds. In benzonitrile, the rate constant for charge recombination is $2.2 \times 10^{10}\ \mathrm{s}^{-1}$, which decreases in THF, a solvent of lower polarity, to $2.7 \times 10^{9}\ \mathrm{s}^{-1}$. In both solvents charge recombination leads to a quantitative recovery of the singlet ground state – no involvement of any triplet excited state (i.e., ZnPc or flavin) is noted.

## Conclusions

We have prepared for the first time a ZnPc-flavin dyad **1** using a Pd-catalyzed cross coupling methodology between appropriately functionalized flavin and Pc chromophores. This donor–acceptor conjugate has been electrochemically and photophysically characterized. Although the two components do not notably interact in the ground state, we have been able to demonstrate photoinduced charge transfer from the Pc to the flavin unit. Remarkable is the fact that the radical ion pair state lifetimes, although short, are still longer than in a recently published ZnPc-$C_{60}$ donor–acceptor conjugate[24] (i.e., benzonitrile: $3.3 \times 10^{10}\ \mathrm{s}^{-1}$; THF: $8.3 \times 10^{9}\ \mathrm{s}^{-1}$). This fact can be rationalized by taking into account that $(\text{flavin})^{\bullet -}$ gains some stabilization based on its polarizability, which is also believed to contribute to retarding a fast charge recombination.[25]

## Experimental

### General Methods and Materials

Chemicals were purchased from commercial suppliers and used without further purification. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å), and TLC on aluminum sheets precoated with silica gel 60 $F_{254}$ (E. Merck). PTFE filters (pore size 0.45 μm) were used. IR spectra were recorded on a Bruker Vector 22 spectrophotometer using KBr disks. Matrix-assisted laser desorpton–ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were determined on a BRUKER REFLEX III instrument equipped with a nitrogen laser operating at 337 nm. NMR spectra were recorded with a Bruker AC-300 instrument. UV/Vis spectra were recorded with a Hewlett–Packard 8453 instrument.

### Photophysics

Femtosecond transient absorption studies were performed with 670 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:sapphire laser system (Clark-MXR, Inc.). Fluorescence lifetimes were measured with a Laser Strobe Fluorescence Lifetime Spectrometer (Photon Technology International) with 337 nm laser pulses from a nitrogen laser fibre-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the Laser Strobe systems are described on the manufacture's website (http://www.pti-nj.com/LaserStrobe/; verified 28 March 2008). Emission spectra were recorded by using a FluoroMax-3 (Horiba Co.). The experiments were performed at 20°C.

### Electrochemistry

CV was performed on a Windows-driven BAS 100w electrochemical analyzer at room temperature with a three-electrode configuration in *o*-dichlorobenzene (*o*-DCB) solution that contained the substrate (typically $\sim$1 mmol $dm^{-3}$) and the supporting electrolyte. A glassy carbon (ϕ 3 mm) disc was used as the working electrode, a platinum wire (ϕ 1 mm), and a commercial Ag/AgCl electrode were the counter and the reference electrodes, respectively. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. Tetrabutylammonium hexafluorophosphate ($n$-$Bu_4NPF_6$) was employed as the supporting electrolyte at a concentration of 0.1 mol $dm^{-3}$. Solutions were stirred and deaerated by bubbling argon for a few minutes before each voltammetric measurement.

### 6-(4-Iodoanilinyl)-3-methyluracile **3**

4-Iodoaniline (0.46 g, 2.1 mmol) and 6-chloro-3-methyluracile (**2**) (0.34 g, 2.1 mmol) were added to a mixture of *N*,*N*-diethylaniline (1 mL) and acetic acid (0.1 mL). After heating at 190°C for 30 min, ether was added to the cold mixture and the precipitate was filtered off. Crystallization from ethanol afforded **3** as brownish needles. Yield: 0.49 g (68%), mp >300°C. (Found: C 38.27, H 2.89, N 12.08%. Calc. for $C_{11}H_9IN_3O_2$: C 38.51, H 2.94, N 12.25%.) $\nu_{max}$ (KBr)/$cm^{-1}$ 3390, 1725, 1692, 1556, 1290, 1182, 980, 752. $\delta_H$ (300 MHz, ($D_6$)DMSO) 8.41 (br s, 1H, ArNH), 7.68 (d, AA′XX′ $J$ 7.2, 2H, ArH), 7.01 (d, AA′XX′ $J'$ 7.2, 2H, ArH), 4.88 (s, 1H, CH), 3.05 (s, 3H, $CH_3$). $\delta_C$ (75 MHz, ($D_6$)DMSO) 202.1 (C=O), 168.5 (C=O), 150.6 (C-7), 137.7 (C-9), 129.9 (C-5), 123.5 (C-6), 118.1 (C-8), 85.7 (C-10), 28.0 ($CH_3$). *m*/*z* (EI) 343 [$M^+$], 216 [$(M - I^+)$].

### 10-(4-Iodophenyl)-3-methylisoalloxazine **4**

In a mixture of $Ac_2O$ and AcOH (4:1, 2 mL), nitrosobenzene (0.32 g, 3 mmol) and 6-(4-iodoanilinyl)-3-methyluracile (**3**) (0.343 g, 1 mmol) were added. The mixture was heated at 140°C for 30 min and the solvent was eliminated under reduced pressure. Ethanol was added to the crude product and the precipitate was filtered off. After flash column chromatography ($SiO_2$, AcOEt/$CHCl_3$ 1:9) **4** was obtained as a yellow solid. Yield: 236 mg (55%), mp >300°C. (Found: C 47.19, H 2.69, N 12.86%. Calc. for $C_{17}H_{11}IN_4O_2$: C 47.19, H 2.69, N 12.86%.) $\nu_{max}$ (KBr)/$cm^{-1}$ 1713, 1672, 1551, 1281, 1173, 984, 750. $\delta_H$ (300 MHz, $CDCl_3$) 8.35 (dd, $J$ 8.6, $J'$ 1.62, 1H, flavin 6-H), 8.01 (d, AA′XX′ $J$ 8.6, 2H, ArH), 7.75–7.55 (m, 2H, flavin 7-H, 8-H) 7.06 (d, AA′XX′ $J$ 8.6, 2H, ArH), 6.93 (dd, $J$ 8.6, $J'$ 1.62, 1H, flavin 9-H), 3.49 (s, 3H, $CH_3$). *m*/*z* (ES) 430 [$M^+$].

### *Tri*-tert-*butyl-[(*E*)-2-(3-methylisoalloxazinyl)-10-styryl]-phthalocyanine Zn*$^{II}$ **1**

A mixture of vinylphthalocyanine **5** (92 mg, 0.12 mmol), 10-(4-iodophenyl)-3-methylisoalloxazine (**4**) (50 mg, 0.12 mmol), LiCl (3 mg, 0.072 mmol), $(MeCN)_2PdCl_2$ (2 mg, 76 μmol), tetrabutylammonium bromide (40 mg, 0.12 mmol), and triethylamine (0.1 mL) in *N*,*N*-dimethylformamide (DMF, 4 mL) was heated under argon at 100°C during 48 h. The solvent was removed under reduced pressure and the crude was triturated with methanol and then filtered off. After flash column chromatography ($SiO_2$, THF/hexane, 1/3), **1** was obtained as a green fluorescent solid. Yield 68 mg (52%), mp >300°C. (Found: C 69.82, H 4.75, N 15.36%. Calc. for $C_{63}H_{52}N_{12}O_2Zn$: C 70.42, H 4.88, N 15.64%.) $\nu_{max}$ (KBr)/$cm^{-1}$ 2956, 1716, 1665, 1615, 1586, 1489, 1317, 1275, 1084, 1046, 921, 806, 748. $\lambda_{max}$/nm (log $\varepsilon$) 690 (5.15), 676 (5.10), 348 (4.90). $\delta_H$ (300 MHz, $CDCl_3$) 9.0–7.0 (m, 22H, ArH, flavin, vinylic), 3.5 (br s, 3H, $NCH_3$), 1.9–1.6 (m, 27H, $C(CH_3)_3$). *m*/*z* (MALDI-TOF) 1072–1080 [$M^+$].

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## References

[1] (a) S. Fukuzumi, in *Functional Organic Materials* (Eds T. J. J. Müller, U. H. F. Bunz) **2007**, p. 465 (Wiley-VCH: Weinheim).
(b) F. D'Souza, O. Ito, *Coord. Chem. Rev.* **2005**, *249*, 1410. doi:10.1016/J.CCR.2005.01.002

[2] N. Martin, *Chem. Commun.* **2006**, 2093. doi:10.1039/B601582B

[3] G. de la Torre, C. G. Claessens, T. Torres, *Chem. Commun.* **2007**, 2000. doi:10.1039/B614234F

[4] (a) K. M. Kadish, K. M. Smith, R. Guilard, (Eds), *The Porphyrin Handbook* **2003**, Vols. 15–20 (Academic Press: San Diego, CA).
(b) G. de la Torre, M. Nicolau, T. Torres, in *Supramolecular Photosensitive and Electroactive Materials* (Ed. H. Nalwa) **2001**, pp. 1–111 (Academic Press: New York, NY).
(c) G. de la Torre, P. Vázquez, F. Agulló-López, T. Torres, *Chem. Rev.* **2004**, *104*, 3723. doi:10.1021/CR030206T

[5] (a) J. G. Xue, S. Uchida, B. P. Ran, S. R. Forrest, *Appl. Phys. Lett.* **2004**, *84*, 3013. doi:10.1063/1.1713036
(b) J. G. Xue, S. Uchida, B. P. Rand, S. R. Forrest, *Appl. Phys. Lett.* **2004**, *85*, 5757. doi:10.1063/1.1829776

[6] (a) E. Palomares, M. V. Martínez-Díaz, S. A. Haque, T. Torres, J. R. Durrant, *Chem. Commun.* **2004**, 2112. doi:10.1039/B407860H

(b) A. Morandeira, I. Lopez-Duarte, M. V. Martínez-Díaz, B. O'Regan, C. Shuttle, N. A. Haji-Zainulabidin, T. Torres, E. Palomares, J. R. Durrant, *J. Am. Chem. Soc.* **2007**, *129*, 9250. doi:10.1021/JA0722980

(c) J.-J. Cid, J.-H. Yum, S.-R. Jang, Md. K. Nazeeruddin, E. Martínez-Ferrero, E. Palomares, J. Ko, M. Grätzel, T. Torres, *Angew. Chem. Int. Ed.* **2007**, *46*, 8358. doi:10.1002/ANIE.200703106

(d) P. Y. Reddy, L. Giribabu, C. Lyness, H. J. Snaith, C. Vijaykumar, M. Chandrasekharam, M. Lakshmikantam, J.-H. Yum, K. Kalyanasundaram, M. Grätzel, M. K. Nazeeruddin, *Angew. Chem. Int. Ed.* **2007**, *46*, 373. doi:10.1002/ANIE.200603098

(e) B. C. O'Regan, I. Lopez-Duarte, M. V. Martinez-Diaz, A. Forneli, J. Albero, A. Morandeira, E. Palomares, T. Torres, J. R. Durrant, *J. Am. Chem. Soc.* **2008**, *130*, 2906. doi:10.1021/JA078045O

[7] (a) J. P. C. Tomé, A. M. V. M. Pereira, C. M. A. Alonso, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro, M. V. Martínez-Díaz, T. Torres, G. M. Aminur Rahman, J. Ramey, D. M. Guldi, *Eur. J. Org. Chem.* **2006**, 257. doi:10.1002/EJOC.200500558

(b) S. Tannert, E. A. Ermilov, J. O. Vogel, M. T. M. Choi, D. K. P. Ng, B. Röder, *J. Phys. Chem. B* **2007**, *111*, 8053. doi:10.1021/JP0724222

(c) Y. Bian, X. Chen, D. Wang, C.-F. Choi, Y. Zhou, P. Zhu, D. K. P. Ng, J. Jiang, Y. Weng, X. Li, *Chem. Eur. J.* **2007**, *13*, 4169. doi:10.1002/CHEM.200601668

[8] (a) D. M. Guldi, J. Ramey, M. V. Martínez-Díaz, A. de la Escosura, T. Torres, T. Da Ros, M. Prato, *Chem. Commun.* **2002**, 2774. doi:10.1039/B208516J

(b) D. M. Guldi, I. Zilbermann, A. Gouloumis, P. Vázquez, T. Torres, *J. Phys. Chem. B* **2004**, *108*, 18485. doi:10.1021/JP047105Z

(c) K. N. Kim, C. S. Choi, K.-Y. Kay, *Tetrahedron Lett.* **2005**, *46*, 6791. doi:10.1016/J.TETLET.2005.08.038

(d) A. de la Escosura, M. V. Martínez-Díaz, D. M. Guldi, T. Torres, *J. Am. Chem. Soc.* **2006**, *128*, 4112. doi:10.1021/JA058123C

(e) B. Ballesteros, G. de la Torre, T. Torres, G. L. Hug, G. M. Aminur Rahman, D. M. Guldi, *Tetrahedron* **2006**, *62*, 2097. doi:10.1016/J.TET.2005.08.126

(f) A. Gouloumis, A. de la Escosura, P. Vázquez, T. Torres, A. Kahnt, D. M. Guldi, H. Neugebauer, C. Winder, M. Drees, N. Serdar, Sariciftci, *Org. Lett.* **2006**, *8*, 5187. doi:10.1021/OL061723B

(g) T. Torres, A. Gouloumis, D. Sánchez-García, J. Jayawickramarajah, W. Seitz, D. M. Guldi, J. L. Sessler, *Chem. Commun.* **2007**, 292. doi:10.1039/B613086K

(h) G. Bottari, D. Olea, C. Gómez-Navarro, F. Zamora, J. Gómez-Herrero, T. Torres, *Angew. Chem. Int. Ed.* **2008**, *47*, 2026 doi:10.1002/ANIE.200705260

[9] A. Gouloumis, D. González-Rodriguez, P. Vázquez, T. Torres, S. Liu, L. Echegoyen, J. Ramey, G. L. Hug, D. M. Guldi, *J. Am. Chem. Soc.* **2006**, *128*, 12674. doi:10.1021/JA055344+

[10] M. S. Rodríguez-Morgade, T. Torres, C. Atienza-Castellanos, D. M. Guldi, *J. Am. Chem. Soc.* **2006**, *128*, 15145. doi:10.1021/JA0622195

[11] D. González-Rodríguez, C. G. Claessens, T. Torres, S. Liu, L. Echegoyen, N. Vila, S. Nonell, *Chem. Eur. J.* **2005**, *11*, 3881. doi:10.1002/CHEM.200400779

[12] (a) B. Ballesteros, S. Campidelli, G. de la Torre, C. Ehli, D. M. Guldi, M. Prato, T. Torres, *Chem. Commun.* **2007**, 2950. doi:10.1039/B702819A

(b) B. Ballesteros, G. de la Torre, C. Ehli, G. M. Aminur Rahman, F. Agulló-Rueda, D. M. Guldi, T. Torres, *J. Am. Chem. Soc.* **2007**, *129*, 5061. doi:10.1021/JA068240N

[13] A. González-Cabello, P. Vázquez, T. Torres, D. M. Guldi, *J. Org. Chem.* **2003**, *68*, 8635. doi:10.1021/JO0341968

[14] A. Koziol, M. M. Szafran, P. F. Heelis, in *Flavins and Flavoproteins* (Eds D. E. Edmondson, D. B. Mccormick) **1987**, pp. 287–290 (Gruyter: Berlin).

[15] F. Müller (Ed.), *Chemistry and Photochemistry of Flavoenzymes* **1991–1992**, Vols. 1–3 (CRC Press: Boca Raton, FL).

[16] A. Sancar, *Annu. Rev. Biochem.* **2000**, *69*, 31. doi:10.1146/ANNUREV.BIOCHEM.69.1.31

[17] (a) Z. Shen, J. Strauss, J. Daub, *Chem. Commun.* **2002**, 460. doi:10.1039/B109151D

(b) Z. Shen, R. Procházka, J. Daub, N. Fritz, N. Acar, S. Schneider, *Phys. Chem. Chem. Phys.* **2003**, *5*, 3257. doi:10.1039/B301279D

[18] (a) J. Takeda, S. Ohta, M. Hirobe, *J. Am. Chem. Soc.* **1987**, *109*, 7677. doi:10.1021/JA00259A017

(b) P. Nayar, A. M. Brun, A. Harriman, T. P. Begley, *Chem. Commun.* **1992**, 395.

(c) K. Hasharoni, H. Levanon, J. Gätschmann, H. Schubert, H. Kurreck, K. Möbius, *J. Phys. Chem.* **1995**, *99*, 7514. doi:10.1021/J100019A037

(d) D. T. Hermann, A. C. Schindler, K. Polborn, R. Gompper, S. Stark, A. B. J. Parusel, G. Grabner, G. Köhler, *Chem. Eur. J.* **1999**, *5*, 3208. doi:10.1002/(SICI)1521-3765(19991105)5:11<3208::AID-CHEM3208>3.0.CO;2-O

[19] F. Yoneda, K. Shinozuka, K. Tsukuda, A. Koshiro, *J. Heterocycl. Chem.* **1979**, *16*, 1365.

[20] G. Nübel, W. Pfleiderer, *Chem. Ber.* **1962**, *95*, 1605. doi:10.1002/CBER.19620950706

[21] A. Gouloumis, S.-G. Liu, A. Sastre, P. Vázquez, L. Echegoyen, T. Torres, *Chem. Eur. J.* **2000**, *6*, 3600. doi:10.1002/1521-3765(20001002)6:19<3600::AID-CHEM3600>3.3.CO;2-S

[22] T. Jeffery, *Tetrahedron Lett.* **1985**, *26*, 2667. doi:10.1016/S0040-4039(00)98131-0

[23] P. F. Heelis, B. J. Parsons, *J. Chem. Soc., Chem. Commun.* **1994**, 793. doi:10.1039/C39940000793

[24] M. Quintiliani, A. Kahnt, T. Wölfle, W. Hieringer, P. Vázquez, A. Görling, D. M. Guldi, T. Torres, *Chem. Eur. J.*, in press. doi:10.1002/CHEM.200701700

[25] E. C. Breinlinger, C. J. Keenan, V. M. Rotello, *J. Am. Chem. Soc.* **1998**, *120*, 8606. doi:10.1021/JA9809556