Perylenediimide—metal ion dyads for photo-induced electron transfer†

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A novel perylene diimide incorporating a tetradentate ligand was synthesized and the photophysical properties of its Cu^+, Cu^{2+}, and Fe^{3+} complexes were investigated by fluorescence experiments.

Understanding photo-induced energy and electron transfers in molecular donor–acceptor systems is crucial for the design of artificial photosynthesis devices. Nature's own photosynthetic reaction centre is by far the most elegant system known and illustrates how carefully oriented molecular arrays of photo- and redox-active components can work in concert to convert and store solar energy.[1] One of us has shown that a dimanganese complex of the ligand N-methyl-N′-carboxymethyl-N,N′-bis(2-pyridylmethyl)ethane-1,2-diamine 1 catalyzes the oxidation of water to dioxygen using a chemical oxidant such as tert-butylhydrogenperoxide.[2] This complex is relevant as a model system for the active site of the oxygen-evolving complex of photosystem II.[3] The challenge is to make the process light-activated as in natural photosynthesis.
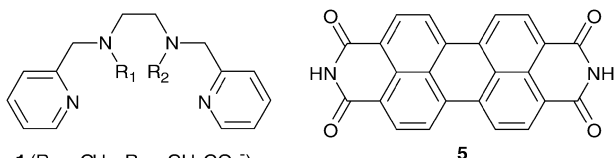
1 ($R_1 = CH_3$, $R_2 = CH_2CO_2^-$)
2 ($R_1 = R_2 = H$), 3 ($R_1 = H$, $R_2 = CH_2Ph$)
4 ($R_1 = CH_2CO_2CH_3$, $R_2 = CH_2Ph$)

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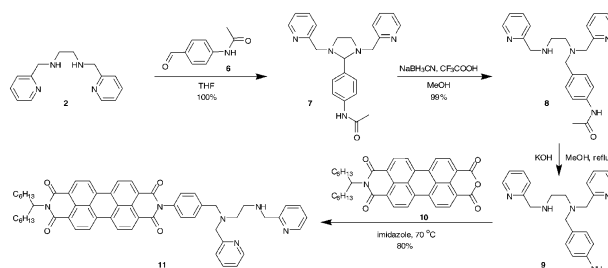
We became interested in combining polydendate ligands such as 1–4 with the strong light-harvestor perylene diimide 5 (PDI). PDIs possess a unique combination of chemical stability, redox properties, excited state reactivity, luminescence emission, and excited state lifetime.[4] Here we present the synthesis of the first such PDI functionalized with a polydendate ligand and the spectroscopic investigations of the photo-induced electron transfer processes that occur upon coordination of metal ions.

The synthesis is shown in Scheme 1. First, N,N′-bis(2-pyridylmethyl)-1,2-ethanediamine 2, prepared according to a literature protocol,[5] was condensed with 4-acetamidobenzal-

dehyde 6 in dry THF at room temperature under an argon atmosphere to afford the imidazolidine derivative 7 in quantitative yield. This compound was then reduced with $NaBH_3CN/CF_3COOH$, hereby opening the imidazolidine ring to provide compound 8 in high yield. Refluxing this compound overnight in MeOH with 10 molar equivalents of KOH resulted in deacetylation to furnish the aniline derivative 9. The strong polarity of this product rendered its purification difficult, and it was condensed directly with N-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide 10, prepared according to Langhals and Jona,[6] in imidazole at 70 °C to afford the ligand-functionalized PDI 11[7] in a yield of 80%. This product exhibits an excellent solubility in chlorinated solvents, such as dichloromethane.

The Cu(II) complex of the ligand 8 and one chloride ligand was precipitated as the hexafluorophosphate salt from a MeOH solution of 8 and $CuCl_2$. Electrospray ionization (ESI) showed peaks at $m/z = 487$ and 451. The first one is assigned to five-coordinated Cu(II) involving both the tetradentate ligand 8 and one chloride ion $[M^+]$ and the second one corresponds to $[M - Cl - H]^+$. The stoichiometry was also ascertained by elemental analysis. Similarly, the Fe(III) complex of 8 incorporating two chloride ligands (according to ESI) was precipitated as the hexafluorophosphate salt from a MeOH solution of 8 and $FeCl_3$. X-Ray crystallographic analyses on complexes of the related tetradendate ligands 3 and 4 (Fig. 1) suggests that the coordination geometry of the five-coordinated Cu(II) complex is likely to be distorted trigonal bipyramidal and that of the hexa-coordinated Fe(III) complex is likely to be distorted octahedral.†

Complexation of either Fe^{3+}, Cu^+, or Cu^{2+} (added as $FeCl_3$, CuCl or CuI and $CuCl_2$ salts, respectively) by 11 in CH_2Cl_2–MeOH (25 : 1) was observed by changes in the ligand absorptions located in the UV-region (250–350 nm). The absorption spectra correspond to a superposition of that of

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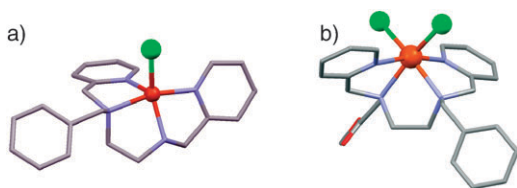

Scheme 1 Synthesis of perylene diimide incorporating a tetradentate ligand.

Fig. 1 X-Ray crystal structures of the cations (a) $[Cu(II)Cl(3)]^+$ and (b) $[Fe(III)Cl_2(4)]^+$. Counter anions are removed for clarity.

the metal complex of **8** alone and that of PDI, *i.e.*, complexation does not alter the PDI absorptions (462, 489, and 527 nm), and, accordingly, the PDI unit can be selectively excited at 489 nm.†

We note that the ability of Fe^{2+} and Fe^{3+} to quench the fluorescence of more electron-rich aryloxy-substituted PDIs has previously been observed *via* coordination of the metal ions to ligand groups, such as terpyridines or amides.[8] Electron-rich amine-substituted PDIs were also reported to undergo photo-induced electron transfer processes efficiently.[9] To address the possibility of photo-induced energy or electron transfer reactions between the PDI unit in **11** and coordinated metal ion, the fluorescence behaviour was studied in dichloromethane solution containing 10% methanol to dissolve the metal salts. Complexation of Fe^{3+}, Cu^+, or Cu^{2+} ions by **11** has a strong quenching effect on the PDI fluorescence with no discernible alteration in peak shape. Upon titration of a dilute solution of **11** (10^{-5} M) with Fe^{3+} (Fig. 2) or Cu^{2+} ions, the steady-state fluorescence follows the Stern–Volmer equation for static quenching, $I_0/I = 1 + K_s[Q]$, where I and I_0 are the integrated emission intensities with and without quencher (Q) present. Within the limited solubility of the metal ions, almost full quenching (<10% intensity left) is obtained. The association constants K_s for complexation of Fe^{3+} and Cu^{2+} were determined to be 178 M^{-1} and 79 M^{-1}, respectively, assuming full quenching at infinite concentration of metal ions. Low inherent fluorescence of $[Fe(III)Cl_2(11)]^+$ and $[Cu(II)Cl(11)]^+$ would increase the resulting K_s by up to 20%, but also introduce deviations from the static quenching equation. The association constant for Cu^+ could not be determined on
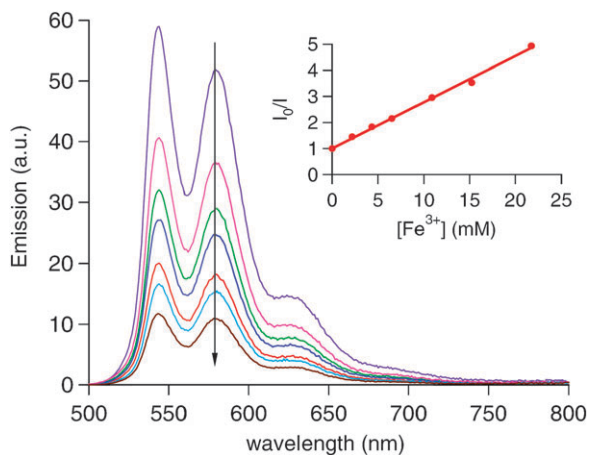
account of the low solubility of CuCl. However, extracting CuCl into a solution of the ligand results in considerable quenching of the PDI fluorescence. Dynamic quenching is ruled out as addition of an excess of either Fe^{3+}, Cu^+, or Cu^{2+} ions to a PDI devoid of the ligand group does not change the fluorescence intensity.

According to simple geometry optimizations, the distance between the PDI center and the metal ion is around 12 Å. Only Cu^{2+} complexes of the tetradendate ligand have an overlapping absorption band with the PDI emission band, but with very low molar absorptivity; $[Cu(II)Cl(3)]ClO_4$ exhibits an absorption band in MeCN at λ_{max} 702 nm with $\varepsilon = 154$ M^{-1} cm^{-1}.† Energy transfer from the excited PDI (PDI*) to the Cu^{2+} metal complex is thus possible, albeit of low probability. For the other metals used, no energetic interaction is possible, and fluorescence quenching in these cases cannot be explained by either Förster or Dexter energy transfer.[10] Instead, the quenching is most likely to occur by an electron transfer process. In the case of Fe^{3+} and Cu^{2+}, this electron transfer should occur from PDI* to the metal ion, while instead Cu^+ is expected to reduce PDI*. Quenching originating from paramagnetic (Fe^{3+} and Cu^{2+}) and/or heavy atom species enhancing the possibility of intersystem crossing[11] seems unlikely: firstly, significant quenching is also observed for the diamagnetic Cu^+ species; secondly, quenching is only observed as the metal ion binds to the ligand.

The redox behaviour of the $[Cu(II)Cl(8)]^+$ and $[Fe(III)Cl_2(8)]^+$ complexes (PF_6^- salts, *vide supra*) was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).[12] The redox potential for $[Cu(II)Cl(8)]^+/[Cu(I)Cl(8)]$ is −0.804 V *vs.* Fc^+/Fc according to DPV, while the redox potential for $[Fe(III)Cl_2(8)]^+/[Fe(II)Cl_2(8)]$ is −0.276 V *vs.* Fc^+/Fc. The CVs of both complexes reveal reversible electrochemistry (Fig. 3). It should be noted that the Fe(III)-complex exhibits more complicated electrochemistry as evidenced by additional shoulders in the CV. The PDI reference compound **12** is reversibly reduced at −1.132 V and −0.872 V *vs.* Fc^+/Fc and irreversibly oxidized at +0.485 V *vs.* Fc^+/Fc. From the measured potentials, it transpires that ground state electron transfer is not possible in either case. However, upon excitation of the PDI unit ($E_0 = 2.35$ eV), the electron donor strength is enhanced considerably; hence concomitant electron transfer to the metal (Cu^{2+} or Fe^{3+})-ligand complex becomes
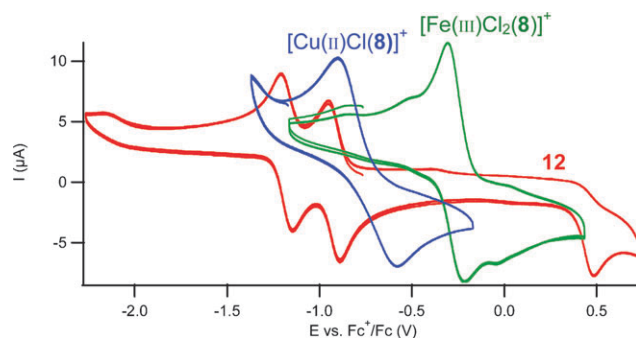

Fig. 2 Fluorescence behaviour upon titration of a dilute solution (CH_2Cl_2 + 10% MeOH) of **11** (10^{-5} M) with Fe^{3+} ions ($FeCl_3$). The arrow represents increasing concentration of Fe^{3+}.

Fig. 3 Cyclic voltammograms of $[Cu(II)Cl(8)]^+$ (blue), $[Fe(III)Cl_2(8)]^+$ (green) (PF_6^- salts), and PDI **12** (red) in DMF with Bu_4NPF_6 (0.2 M) as supporting electrolyte. Scan rate: 0.1 V s^{-1}.

favourable with a driving force of more than 1 eV. Similarly, the acceptor strength of the excited PDI is also enhanced, and electron transfer from the Cu^+ complex is now a favorable process by more than 2 eV.

In conclusion, by covalently attaching a tetradentate ligand to PDI, metal ions can be brought into close proximity to the PDI unit. While complexation of metal ions (Cu^+, Cu^{2+}, Fe^{3+}) does not perturb the PDI absorption, the fluorescence of compound **11** is partly quenched. The exact mechanism will be the subject to detailed time-resolved spectroscopic studies in future work, but is most likely owing to photo-induced electron transfer. This is promising in view of the ultimate goal to explore derivatives of **11** for light-induced water splitting. We are currently aiming at the related compound containing a carboxylate arm as in compound **1** in order to prepare the hereby dimanganese complex analogous to that reported to catalyse water oxidation.[2] In addition, preliminary experiments reveal that the Cu^{2+} complex of the ligand **8** can be employed for oxidative homo-coupling of phenylacetylene in the presence of O_2 (Glaser coupling), requiring, however, NaH as base for deprotonation of the alkyne. The possibility for light-driven alkyne dimerization, under oxygen-free conditions, using the PDI-functionalized Cu^{2+} complex is another interesting aspect to be pursued in the future.

Notes and references

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7 Preparation of compound **11**: Compound **8** (658 mg, 1.69 mmol) was dissolved in abs. EtOH (5 mL), and KOH (289 mg, 5.15 mmol) was added. The mixture was refluxed overnight, then cooled to rt, and aqueous HCl (2 M) was added until pH $\sim$ 7. The resulting precipitate was removed by filtration, and the filtrate was concentrated *in vacuo* to provide the product **9** that was then ground together with **10** (300 mg, 0.53 mmol) and imidazole (1.0 g) to a homogenous powder. The mixture was heated at 70 °C, then cooled to rt and dissolved in MeOH. Water was added, the resulting precipitate was collected by centrifugation, washed with water, and dried under vacuum. The product **11** was hereby obtained as a dark red solid (383 mg, 80%). M.p. 115 °C (dec.). ^{1}H-NMR (CDCl$_3$, 300 MHz): δ = 0.80–0.843 (m, 4H), 1.22–1.86 (m, 12H), 1.80–1.88 (m, 4H), 2.18–2.35 (m, 4H), 2.82–2.85 (m, 2H), 2.92–3.00 (m, 2H), 3.72 (s, 2H), 3.76 (s, 2H), 4.00 (s, 2H), 5.10–5.20 (m, 1H), 7.03–8.58 ppm (m, 20H). HR-MS (FAB$^+$): m/z = 903.4587 $[M + H]^+$; $C_{58}H_{59}N_6O_4$ requires: 903.4598.
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12 Cyclic and differential pulse voltammetries were measured using a glassy carbon working electrode and a Pt wire counter electrode. All potentials are expressed relative to that of Fc^+/Fc (0.31 V *vs.* SCE; A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, Inc., Cambridge, UK, 2nd edn, 2001.