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Strong intramolecular electronic interactions in an anthraquinone bridged bis-ethenylphthalocyaninatozinc(II) triad

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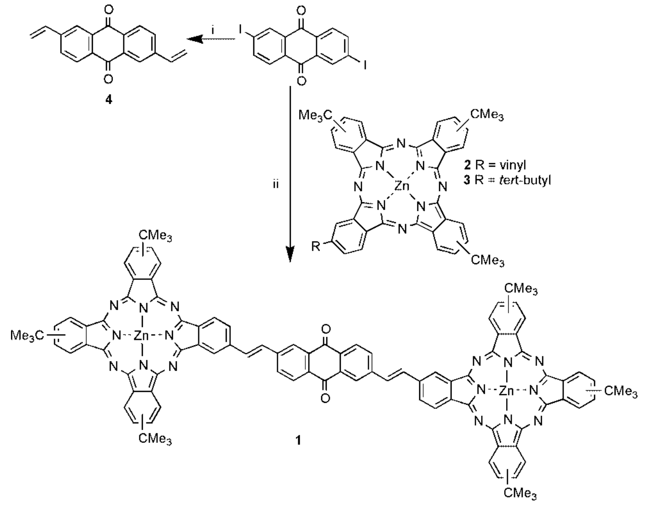
Two metallophthalocyanines bridged by ethenyl spacers to an anthraquinone moiety have been synthesized; both spectroscopic and electrochemical experiments have demonstrated strong intramolecular electronic interactions between the phthalocyanine donors and the anthraquinone acceptor unit.

There has been a great deal of recent research on the properties of phthalocyanine (Pc)-based molecular assemblies for the construction of new molecular materials.[1] However, few systems possess sufficient structural constraints to influence the factors that control electron transfer processes between the donor and acceptor moieties. [2–4] We describe here the synthesis and electrochemical behaviour of an anthraquinone (AQ) covalently linked by ethenyl spacers with two tri-*tert*-butylphthalocyaninatozinc(II) moieties **1**[†] (Scheme 1), for the study of intramolecular electronic interactions between the Pc donor and AQ acceptor.

The synthesis was carried out by palladium-catalysed Heck-type coupling between tri-*tert*-butylvinylphthalocyaninatozinc(II) (**2**)[5a] and 2,6-diiodo-9,10-anthraquinone, which was in turn prepared by a double Sandmeyer reaction from commercially available 2,6-diamino-9,10-anthraquinone. The model compound, 2,6-divinyl-9,10-anthraquinone, **4**, has been prepared for comparison by a Stille coupling reaction.[6]

The UV–Vis spectrum of triad **1** in THF shows a split Q-band at 696 and 675 nm, and a Soret band at 352 nm (Fig. 1). Splitting of the Q-band in this case could be attributed to an effect of 'local asymmetry' in the molecule.[5b] Importantly, comparing the spectra with those of the model compound **2** (675, 351 nm) and tetra-*tert*-butylphthalocyaninatozinc(II) **3** (672, 348 nm) reveals a very significant red shift of about 21 and 24 nm for the Q-bands with respect to **2** and **3**, respectively. This indicates a substantial extension of the π system in triad **1**. If this is correct, there may also be strong intramolecular electronic interactions between the electron-donating Pc moiety and the acceptor AQ unit. This is perfectly supported by the electrochemical analysis discussed below.



Scheme 1 Synthesis of bis(tri-*tert*-butylphthalocyanine)–anthraquinone triad **1**, and 2,6-divinylanthraquinone **4**. *Reagents and conditions*: i, tributyl(vinyl)tin, $Pd(PPh_3)_4$, toluene, 100 °C; ii, $(MeCN)_2PdCl_2$, Bu_4NBr, Et_3N, toluene, 100 °C.

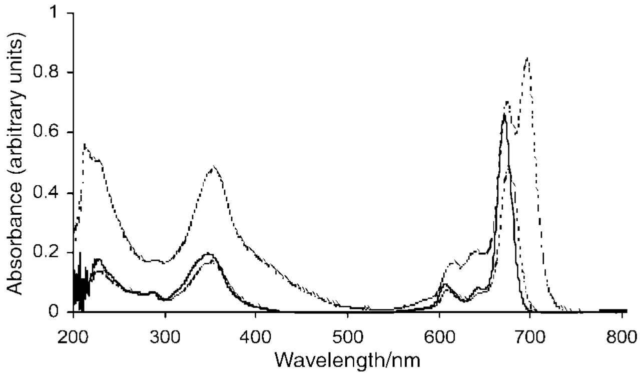


Fig. 1 Electronic spectra of **1** (dashed line), **2** (dotted line) and **3** (solid line) in THF. [C] *ca.* 1×10^{-5} mol L^{-1}.

Solution electrochemistry of triad **1** and model compounds **2**, **3**, **4** and AQ in THF was studied by cyclic voltammetry (CV) and Osteryoung square voltammetry (OSWV). The voltammetric results are summarised in Fig. 2 and Table 1. As shown in Fig. 2, the CV of triad **1** shows that it is electrochemically active in both anodic and cathodic sweep directions between +1.2 and −3.0 V. In the anodic scan, all the redox processes are Pc-based because no oxidations can be observed for either AQ or its derivative **4** in this potential region. In the cathodic scan, triad **1** exhibits five reduction waves. Fig. 2 shows that the first wave is a chemically irreversible process when swept to −0.84

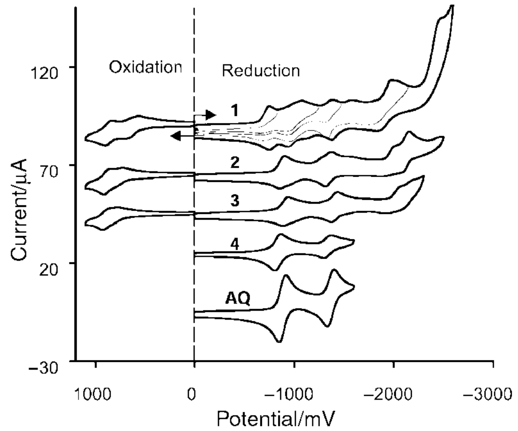


Fig. 2 CVs (0.1 V s^{-1}) for compounds **1**, **2**, **3**, **4** and AQ in THF–$TBAPF_6$ system at room temperature.

Table 1 Electrochemical data (mV *vs*. Ag/AgCl) for the redox processes of compounds **1**, **2**, **3**, **4**, AQ and **2** + AQ (1 : 1) detected by OSWV in THF solution (0.1 mol dm^{-3} TBAPF$_6$) at room temperature under identical experimental conditions[a]

	E^1_{ox}[b]	E^2_{ox}[b]	E^1_{red}[b]	E^2_{red}[c]	E^3_{red}[b]	E^4_{red}[c]	E^5_{red}[b]	E^6_{red}[b]	E^7_{red}[d]
1	652	868	−764	−1076[e]	−1076[e]	−1376	−2024		−2472
2	790	876	−876		−1336		−2008		−2154
3	912[f]		−912		−1404		−2064	−2620	
4				−840		−1348			−2620
AQ				−884		−1384			
2 + AQ	612	808	−864[g]	−864[g]	−1288	−1428	−1984[h]		−1984[h]

[a] OSWVs were obtained using a sweep width of 25 mV, a frequency of 15 Hz, a step potential of 4 mV, and a quiet time of 2 s on a Windows-driven BAS 100w electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN). [b] Pc-based. [c] AQ-based. [d] Pc- and vinyl-based. [e] First AQ and second Pc potentials overlapped. [f] Two-electron process. [g] First Pc and AQ potentials overlapped. [h] Third Pc and Pc-vinyl potentials overlapped.

V at 100 mV s^{-1}, and the process can be assigned to a Pc-based reduction when compared to the results observed for the models **2**, **3**, **4** and AQ. Thus, on the whole, this is a chemically irreversible Pc-based two-electron process (1e per Pc moiety). When the sweep (100 mV s^{-1}) is extended cathodically to −1.5 V, a second reduction process is observed which is chemically reversible but electrochemically irreversible (ΔE_p = 146 mV), and it can be assigned to an overlap of the first AQ-based and the second Pc-based reductions based on direct comparison, for a total of three electrons. Similarly, the next two cathodic processes are assigned to the second AQ-based one-electron process (ΔE_p = 82 mV) and to the third Pc-based electrochemically irreversible reduction, respectively. The fifth reduction process, which is chemically irreversible, can either be assigned to the Pc moiety or to the vinyl groups, but a definitive assignment based solely on comparisons with the model compounds is not possible.

Interestingly and most importantly, all of the measurements discussed above show that the redox behaviour of both the Pc and AQ moieties in triad **1** significantly changed when compared to those of the model compounds, indicating strong electronic interactions (inter- and/or intra-molecular) between the donating Pc and the acceptor AQ at ambient conditions. In the case of intermolecular interactions, a control experiment with an equimolar solution of model compounds **2** and AQ was performed. The results indicate, to some degree, the presence of intermolecular electronic interactions between the electron acceptor AQ and the electron Pc donor **2** since there are some changes in both AQ- and Pc-based redox processes (Table 1). This is not surprising because Pcs are known to self-aggregate as well as with other molecules in solution and in the solid state. Recent results published by us for the [60]fullerene–Pc dyads also showed similar intermolecular electronic interactions.[5a] Although some intermolecular effects are visible, pronounced differences between triad **1** and the mixture **2** + AQ are observed, Table 1, especially for the reduction processes. However, the differences for the reductions between the mixture and models **2** or **3** are much smaller. This means that strong intramolecular electronic interactions are present in triad **1** (compare data in Table 1).

In conclusion, the redox potentials of both Pc and AQ moieties in **1** were significantly changed when compared to the related models, showing some degree of intermolecular electronic interactions, but mainly strong intramolecular electronic interactions between the covalently bonded electron-donating Pc and the accepting AQ moieties at ambient conditions in the ground state. This results in a pronounced negative potential shift for the AQ-based reductions and significant positive potential shift for the Pc-based reductions in triad **1**. Owing to the significant extension of the conjugation as evidenced by the large red shift for the Q-bands, the Pc-based oxidations are negatively shifted.

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Notes and references

† *Selected data* for **1**: ν_{max} (KBr)/cm^{-1}: 2953, 1672 (C=O), 1613, 1585, 1486, 1392, 1304, 1255, 1146, 1088, 1047, 920, 831, 747. δ_H(THF, 300 MHz): 9.6–7.6 (m, 34H, arom and vinyl), 2.1–1.8 (m, 54H, Bu^t). MALDI-TOF: *m/z* 1744–1753 [M$^+$]. Elem. Anal. for $C_{106}H_{88}N_{16}O_2Zn_2$: Calc. C, 72.81; H, 5.07; N, 12.82: Found: C, 72.27; H, 4.98; N, 12.33%. UV–Vis (THF): λ_{max}/nm (log ε) = 696 (5.18), 675 (5.10), 352 (4.94).

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