Synthesis of a β-Linked Porphyrin Dimer and some Homo-, and Hetero-bimetallic Complexes
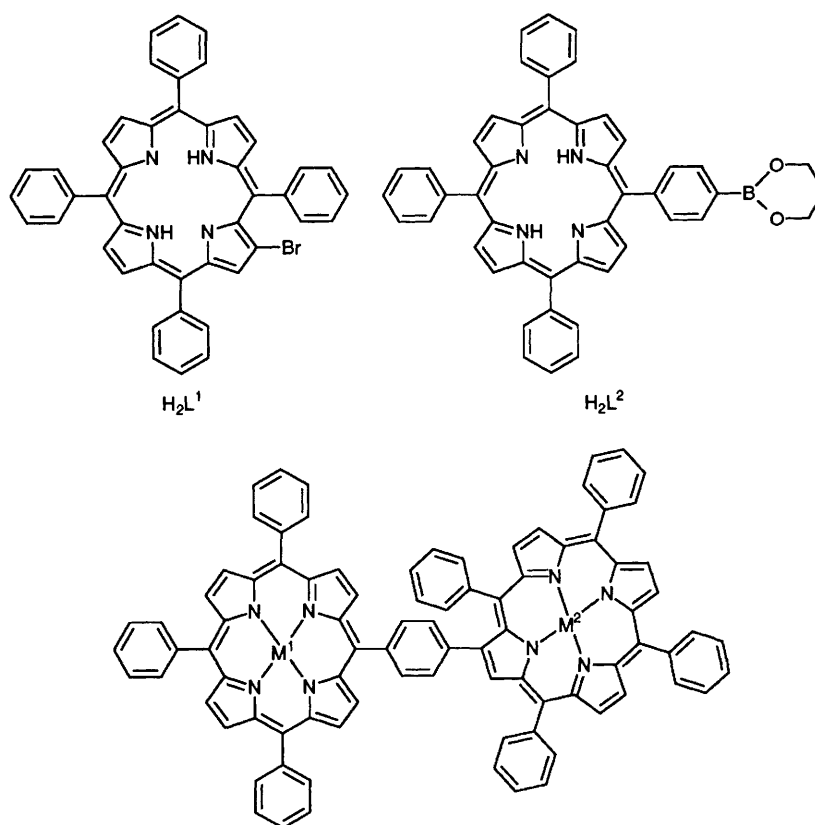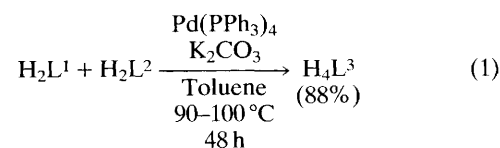
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The porphyrin boronate H_2L^2 undergoes Suzuki cross-coupling reaction with β-monobromoporphyrin H_2L^1 to give the unsymmetrically substituted porphyrin dimer H_4L^3 in high yield; homo-, and hetero-bimetallic complexes of H_4L^3 are prepared.

Porphyrin dimers and their metal complexes have been used as important biomimics for photosynthetic centres,[1,2] and electrocatalysts for O_2 reduction.[3] As synthetic models to aid in the understanding of the dimeric porphyrin-like nature of the electron donor in chlorophyll and for the active sites of water oxidation in photosynthetic system II, a variety of porphyrin dimers with different geometries and separation distances have been synthesized. These include linear or loosely stacked dimers[1] and cofacial dimers.[2] Binuclear metal complexes of such systems have exhibited highly interesting electrocatalytic properties through cooperativity of the metal centres.[2,3] However until now, all such reported dimers are only obtainable *via* long and tedious synthetic procedures and are generally linked *via meso* aryl linkages. We report herein our initial results of a facile method to synthesize a porphyrin dimer linked *via meso-* and β-positions by a phenylene linker *via* Suzuki cross-coupling.[4] We have also synthesized new dimeric homo-, and hetero-metalloporphyrins (Fig. 1).
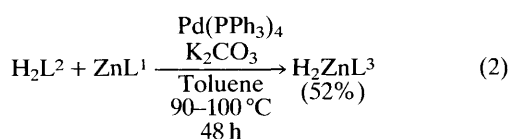
Encouraged by our success in synthesizing β-substituted porphyrins by Suzuki cross-coupling,[5] we envisaged that a porphyrin dimer would be obtained from the coupling of monobromoporphyrin H_2L^1 and boronate porphyrin H_2L^2. The porphyrin boronate H_2L^2 was prepared in 33% yield from the condensation of *p*-(1,3-dioxaborane)benzaldehyde (1 equiv.)–benzaldehyde (3 equiv.) with pyrrole (4 equiv.) in $CHCl_3$ at room temp. for 24 h under N_2 in the presence of a catalytic amount of TsOH.[6] Porphyrin H_2L^1 underwent a smooth Suzuki cross-coupling reaction with H_2L^2 to give a high yield (88%) of the unsymmetically substituted porphyrin dimer H_4L^3 [eqn. (1)].

$$H_2L^1 + H_2L^2 \xrightarrow[\substack{\text{Toluene} \\ 90\text{--}100\,°\text{C} \\ 48\,\text{h}}]{\substack{Pd(PPh_3)_4 \\ K_2CO_3}} H_4L^3 \quad (88\%) \qquad (1)$$

H_2L^1

H_2L^2

	M^1	M^2
H_2L^1	2H	2H
H_2ZnL^3	2H	Zn
Zn_2L^3	Zn	Zn
$CoZnL^3$	Co	Zn
Co_2L^3	Co	Co
Ni_2L^3	Ni	Ni

Fig. 1

Homobinuclear, mononuclear and heterobinuclear complexes of the porphyrin dimer H_4L^3 have been successfully prepared. The homobinuclear complexes were prepared in 76–95% yields from corresponding metal acetates in $CHCl_3$–MeOH at room temp. or in refluxing DMF. The synthesis of heterobimetalloporphyrins required selective monometallation. When $Zn(OAc)_2 \cdot 2H_2O$ (1 equiv.) in methanol was added to H_4L^3 (1 equiv.) in $CHCl_3$ at room temp. in one portion, both H_4L^3 and Zn_2L^3 were obtained. By contrast, when a methanolic solution of $Zn(OAc)_2$ was slowly added to H_4L^3 in $CHCl_3$ at room temp. (1 drop every 5 min), the major product was found to be H_2ZnL^3 (76% yield based on consumed H_4L^3). Metallation was found to be selective at the β-substituted porphyrin core and the structure of H_2ZnL^3 was confirmed by independent synthesis through the cross-coupling of H_2L^2 with ZnL^1 [eqn. (2)].

$$H_2L^2 + ZnL^1 \xrightarrow[\substack{\text{Toluene} \\ 90\text{–}100\,°C \\ 48\,\text{h}}]{\substack{\text{Pd(PPh}_3)_4 \\ K_2CO_3}} \underset{(52\%)}{H_2ZnL^3} \quad (2)$$

UV–VIS spectra of H_4L^3, H_2ZnL^3, Zn_2L^3 and $CoZnL^3$ show split Soret bands. Those of H_4L^3 ($\lambda_{max} = 418$ and 426 nm) were red-shifted compared to those of H_2tpp^5 ($\lambda_{max} = 418$ nm). Complexes Co_2L^3 ($\lambda_{max} = 412$ nm, band width at half height = 33 nm) and Ni_2L^3 ($\lambda_{max} = 422$ nm, band width at half height = 38 nm) showed broadened Soret bands likely due to the expansion of porphyrin ring π-system through excitonic interaction. Emission spectra reveal that $CoZnL^3$ shows a much weaker fluorescence compared to that of H_4L^3, H_2ZnL^3 and Zn_2L^3 possibly by fluorescence quenching via an electron transfer pathway.

Footnote

† All new compounds have been characterized by ^{1}HNMR, MS, UV–VIS spectroscopy and elemental analyses. H_4L^3: δ_H(CDCl$_3$; 250 MHz) -2.74 (s, 2 H), -2.49 (s, 2H), 7.24 (dd, J 7.4, 7.7, 2 H), 7.72 (m, 21 H), 8.00 (d, J 9, 2 H), 8.26 (m, 14 H), 8.93 (m, 15 H); UV, λ_{max} (nm, log ε) 418 (5.38), 426 (5.39), 516 (4.28), 592 (3.76), 648 (3.70); FAB MS (nba matrix) m/z 1227 (M^+–1) (Found: C, 85.00; H, 4.80; N, 8.85. $C_{88}H_{58}N_8 \cdot H_2O$ requires C, 84.85; H, 4.85; N, 9.00%. $CoZnL^3$: UV, λ_{max} (nm, log ε) 423 (5.20), 550 (4.67); FAB MS (nba matrix) m/z 1347 (M^+) (Found: C, 75.75; H, 4.85; N, 7.35. $C_{88}H_{54}N_8$-$CoZn \cdot 2.5CH_3OH$ requires C, 76.15; H, 4.50; N, 7.85%).

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