Synthesis, Characterization, and Electrochemical Studies of β,β'-Fused Metallocenoporphyrins

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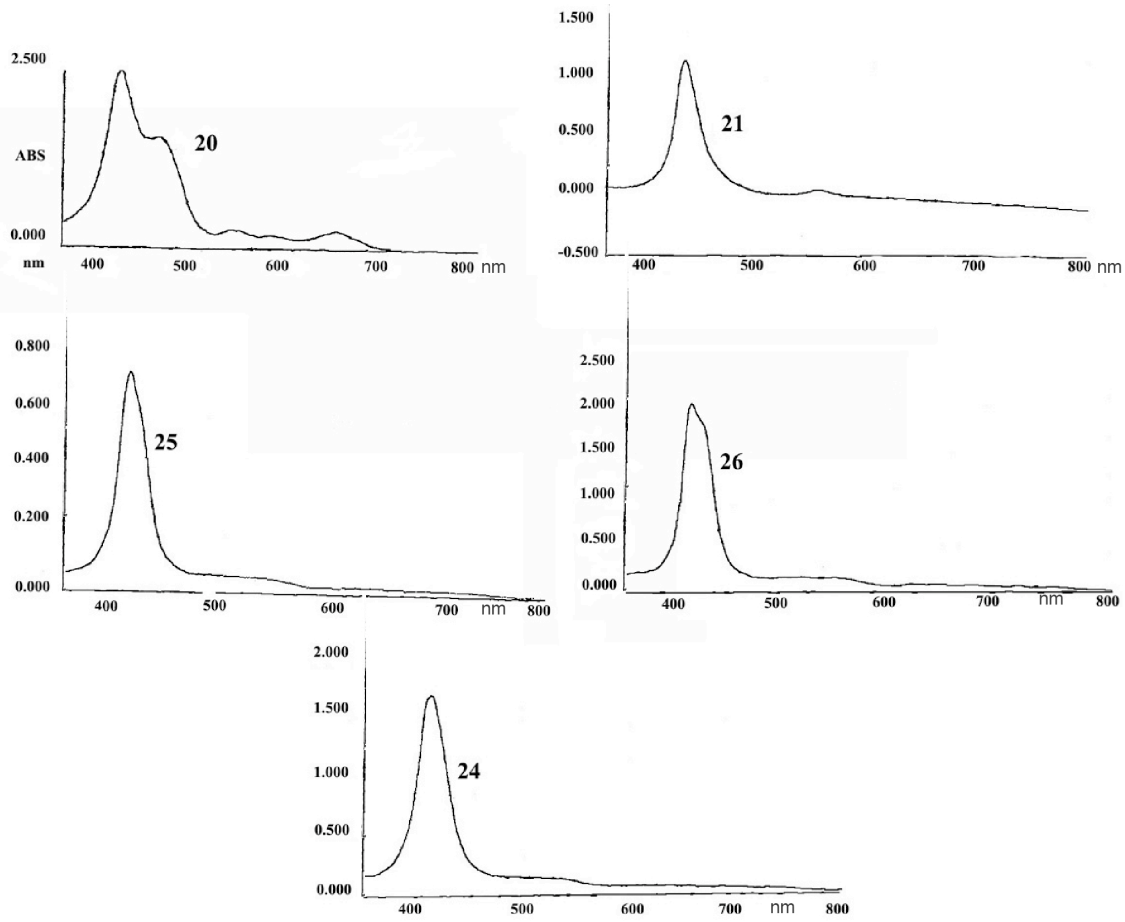

Figure S1. UV/Visible spectra ($CHCl_3$) of bisporphyrinatoferrocenes (**24**-**26**) and mono-ruthenocenoporphyrins (**20**, **21**)

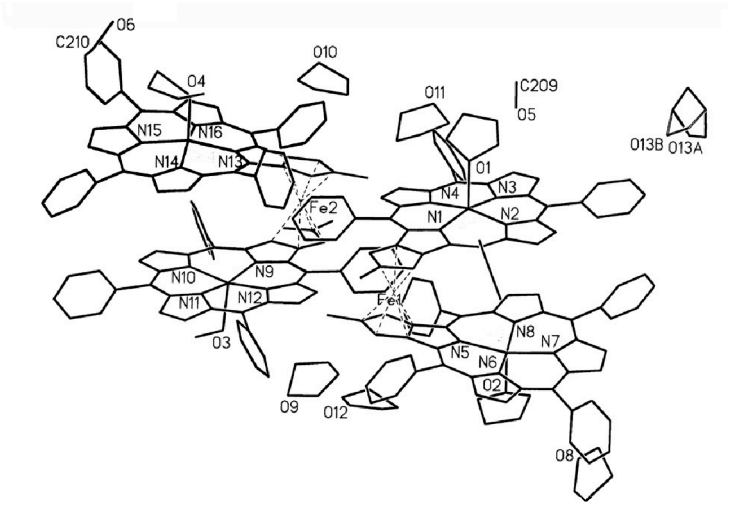

Figure S2. X-Ray crystal structure of bisporphyrinatoferrocene **26**: showing molecules in one asymmetric unit.

Table S1. Half-wave Potentials (V vs SCE) in PhCN Containing 0.1 M TBAP.

compound	oxidation				reduction		$\Delta E_{1/2}$[d]	ref
	Por-centered		Mc-centered		Por-centered		(V)	
(TPP)Ni		1.12[a]			-1.23	-1.78	2.35	6
Ruthenocene				0.60-0.78[b]				7-9
Ferrocene				0.49				*tw*
Ni **2**		1.13[a]			-1.31	-1.85	2.44	*tw*
Ni **13**	1.19	0.99			-1.36	-1.95	2.35	*tw*
Ni **20**		1.09	0.93[c]	0.58	-1.32		2.25	*tw*
Ni **24**	1.22[a]	1.22[a]		0.39	-1.24, -1.35		2.46	*tw*
(TPP)Cu	1.31	1.02			-1.28	-1.73	2.30	6
Cu **25**	1.17[a]	1.17[a]		0.40	-1.38[a]	-1.87[a]	2.55	*tw*

[a]Two one-electron overlapping processes. [b]Irreversible two-electron process. The reported potentials are 0.60 V vs SCE in CH_3CN, 0.1 M $TBABF_4$ (ref 7), 0.69 V vs $Ag/AgClO_4$ in CH_3CN, 0.2 M $LiClO_4$ (ref 8) and 0.78 V vs SCE in CH_3CN, 0.1 M $TBABF_4$ (ref 9), respectively. [c]E_{pa} at a scan rate of 0.1 V/s. [d]HOMO-LUMO gap, the potential difference between the first porphyrin-centered reduction and oxidation. *tw* = this work.