Table S1. Percent Contribution and the Overlap[a] of Iron, Porphyrin and Cyanopyridine Fragments to Selected Orbitals (Based on Mulliken Population Analysis per MO) of $[Fe(P)(CNPy)_2]^+$, Where P is the Porphin with Saddled Deformation (Displacement of β-C from the Porphyrin Mean Plane is 1.176 Å)

	E(eV)	Fe^{3+}	P^{2-}	2 CNPy	$<Fe^{3+}\|P^{2-}>$	$<Fe^{3+}\|CNPy>$	$<P^{2-}\|CNPy>$
$20b_2$	-5.484	63.5 (d_{x2-y2})	26.1, 12.4 ($9b_2$-a_{2u}, $8b_2$)		-0.147	0.000	0.000
26e	-6.249	7.6 (dπ)	90.1 (15e-π*)		-0.015	0.000	0.001
$20a_1$	-6.279	71.9 (d_{z2})	6.7 ($8a_1$)	19.8 ($9a_1$)	0.010	-0.126	-0.036
25e	-7.760	71.1 (dπ)	14.4, 6.9 (13e-π, 14e)		-0.028	-0.001	0.001
$19b_2$	-8.220		47.8,36.7, 7.9 ($9b_2$-a_{2u}, $8b_2$, $7b_2$)	3.9 ($9b_2$)	0.002	-0.003	-0.019
$8b_1$	-8.240	45.0 (d_{xy})	51.9 ($6b_1$-a_{1u})		-0.021	0.000	-0.001
$7b_1$	-8.652	47.0 (d_{xy})	46.3 ($6b_1$-a_{1u})		0.007	0.000	-0.001
24e	-9.638	11.9 (dπ)	45.2, 15.7 (13e-π, 14e)	16.9 (9e)	0.023	-0.005	-0.007
$18a_1$	-10.619	15.4 (d_{z2})		67.0, 7.7 ($9a_1$, $8a_1$)	0.002	0.044	-0.007
$15b_2$	-11.740	16.0 (d_{x2-y2})	41.6, 25.6, 10.3 ($6b_2$, $8b_2$, $9b_2$-a_{2u})		0.035	-0.002	-0.007
$14b_2$	-12.674	10.6 (d_{x2-y2})	49.9,10.8, 10.4, 7.8, 6.8 ($6b_2$, $8b_2$, $5b_2$, $4b_2$,$9b_2$-a_{2u})		0.029	0.000	-0.001

[a] To a first order approximation, positive overlap indicates bonding and negative overlap correlates to antibonding interaction between fragments.[12,]

Table S2. Correlation Table for the Molecular Orbitals of Metalloporphyrin[a]

	D_{4h}	D_{2h}	D_{2d}[b]	C_{4v}	C_{2v}
Metal					
d_{x2-y2}	b_{1g}	a_g	$b_2(b_1)$	b_1	$a_1(a_2)$
d_{z2}	a_{1g}	a_g	a_1	a_1	a_1
d_{xz}, d_{yz}	e_g	b_{2g}, b_{3g}	e	e	b_1, b_2
d_{xy}	b_{2g}	b_{1g}	$b_1(b_2)$	b_2	$a_2(a_1)$
Porphyrin					
LUMO	e_g	b_{2g}, b_{3g}	e	e	b_1, b_2
HOMO	a_{1u}	a_u	b_1	a_2	a_2
	a_{2u}	b_{1u}	b_2	a_1	a_1
HOMO-1	e_g	b_{2g}, b_{3g}	e	e	b_1, b_2

[a] Defining *x* and *y* axes as lying in the porphyrin plane along trans pyrrole nitrogens. [b] Symmetry representations for ruffle-shaped deformation are given in the parentheses.