Electrochemical and photophysical properties of novel ferrocene-based fulleropyrrolidines and fulleropyrrolidinium salts with different aromatic bridge

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There has been a growing interest to synthesize various donor-bridge-acceptor system in which intramolecular charge transfer interaction eventually produces an efficient and long-lived photoinduced charge seperation.[1-4) In these systems the through bond interaction via the bridge mainly depends on the nature of the bridge such as conjugation, rigidity and distance, as well as the strength of the donor- and acceptor moieties.

In line with these aspects, we report herein the synthesis of six novel ferrocene-based donor-acceptor dyads **1**—**6** with different aromatic bridges such as benzene, thiophene, and furan. All new compounds were fully characterized by ^{1}H-NMR, ^{13}C-NMR, IR, UV/Vis and mass spectra.

Electrochemical properties of cmpounds **1**—**6** were measured and compared with compounds **7** and **8** by cyclic voltammetry(CV) together with differential pulse voltammetry(DPV), and the results were collected in Table 1.

Time-resolved transient absorption spectra of the different dyads **1**, **3**, **5** were measured by pico-second laser photolysis in toluene and benzonitrile. We also observed the fluorescence quenching of the dyads by the steady state fluorescence spectra and the pico-second time-correlated single photon counting, and proposed the electron transfer kinetics of the dyads to explain the data. The resonance effect of the bridge plays major role to improve the electron transfer quantum yield in these dyad systems. However, the solvent polarity plays no siginificant role in these systems.

Reference

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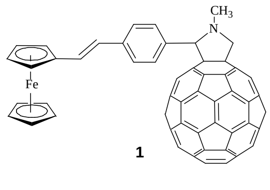

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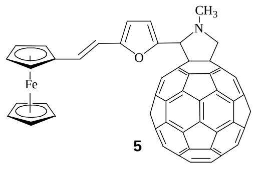

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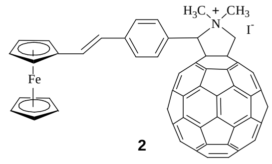

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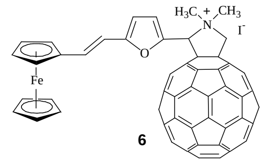

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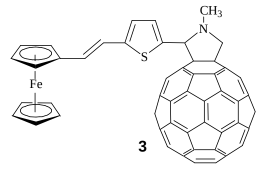

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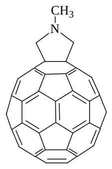

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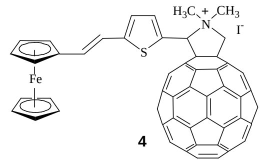

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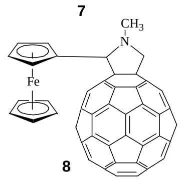

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Table 1. Electrochemical properties of **1 – 8,** Values for $(E_{PC}+E_{PA})/2$[V], Carbon electrode/Ag /Ag$^+$, 0.1 M TBABF$_4$ THF, scan rate 100 mV/s, T = 25 ℃

	1	2	3	4	5	6	7	8
Ox	0.73	0.81	0.80	0.80	0.71	0.82		0.84
Red	-0.28	-0.16	-0.34	-0.04	-0.19	-0.03	-0.17	-0.23
	-0.86	-0.72	-0.90	-0.14	-0.77	-0.55	-0.75	-0.80
	-1.47	-0.90	-1.64	-0.54	-1.40	-0.73	-1.38	-1.43
	-1.93	-1.36	-1.86	-0.73	-1.86	-1.15	-1.85	-1.88
	-2.29	-1.67	-2.16	-1.34	-2.26	-1.49		
	-2.64	-1.82		-1.50	-2.56	-1.82		
		-2.17		-1.71				
		-2.52						

Table 2. Photophysical properties of compounds **1, 3, 5, 7, 8** in toluene and benzonitrile

Compound	Φ (in toluene)	K_{ET}
7	6.0×10^{-4}	
1	2.6×10^{-5}	1.5×10^{10}
3	2.0×10^{-5}	1.9×10^{10}
5	1.0×10^{-4}	3.3×10^{9}
8	3.9×10^{-5}	9.6×10^{9}
Compound	Φ (in benzonitrile)	K_{ET}
7	6.0×10^{-4}	
1	3.6×10^{-5}	9.0×10^{9}
3	1.7×10^{-5}	2.0×10^{10}
5	7.7×10^{-5}	3.9×10^{9}
8	4.4×10^{-5}	7.2×10^{9}

$$\Phi_f = \frac{k_f}{k_f + k_{IC} + k_{ISC} + k_{ET}}\ k_f\tau_f$$

$$k_{ET} = 1/\tau - 1/\tau_{ref} = (\Phi_{ref}/\Phi - 1)/\ \tau_{ref}$$