

*Photophysical characterization of a cytidine-guanosine tethered
phthalocyanine-fullerene dyad*

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Supporting Information

- I. Electrochemical Analysis
- IIa. Estimation of Driving Force
- IIb. Photophysical Studies

I. Electrochemical Analysis

Cyclic voltammetry and Osteryoung square wave voltammetry (OSWV) analyses were carried out using an Autolab PGStat 30 potentiostat with analytical electrochemical software. Measurements were made at room temperature using a three-electrode configuration in dichloromethane (DCM) solutions containing the substrate (typically about 1 mmol dm^{-3}) and the supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF₆) at a 0.05 mol dm^{-3} concentration. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. A glassy-carbon disc ($\varnothing 3 \text{ mm}$) was used as the working electrode after being polished with alumina ($0.3 \mu\text{m}$). A platinum wire ($\varnothing 1 \text{ mm}$) was used as the counter electrode and an Ag/AgNO₃ commercial electrode was used as the reference electrode. The samples were purged with argon prior to each measurement. The scan rate was 100 mV s^{-1} unless otherwise specified. 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 seconds .

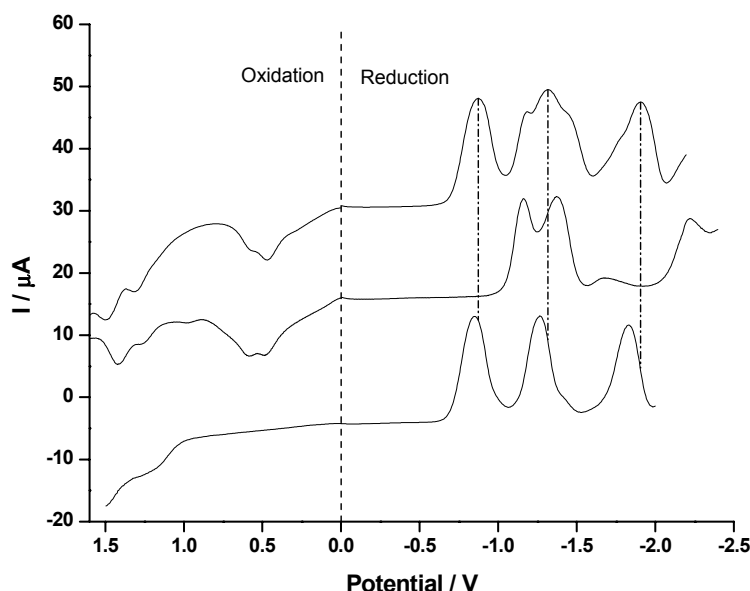


Figure S1. OSWVs for **1**, **2** and **3** (from top to bottom) in DCM-TBAPF₆ solution at room temperature.

	$E_{\text{red}}^{1[\text{a}]}$	$E_{\text{red}}^{2[\text{b}]}$	$E_{\text{red}}^{3[\text{a}]}$	$E_{\text{red}}^{4[\text{b}]}$	$E_{\text{red}}^{5[\text{a}]}$	$E_{\text{ox}}^{1[\text{b}]}$	$E_{\text{ox}}^{2[\text{b}]}$	$E_{\text{ox}}^{3[\text{b}]}$	$E_{\text{ox}}^{4[\text{b}]}$
1	-0.87	-1.17	-1.32	-1.38	-1.90	0.47	0.57	1.31	1.50
2		-1.16		-1.37	-2.22 ^[b]	0.49	0.58	1.42	
3	-0.85		-1.26		-1.83			1.30 ^[c]	

Table S1. Summary of the electrochemical data (V vs Ag/AgNO₃) for the redox processes of compounds **1**, **2** and **3** as detected by OSWV in DCM solution (0.05 mol dm⁻³ TBAPF₆) at room temperature. Note: [a] C₆₀-based reduction, [b] Pc-based redox process, and [c] pyrrolidine-based oxidation. Errors are estimated at less than 2 mV in all OSWV measurements.

IIa. Estimation of Driving Force

Estimation of ΔG°_{ET}

$$\Delta G_{CS}^{\circ}/eV = e[E^{\circ}(D^{+}/D) - E^{\circ}(A/A^{\cdot})] - E_{00} \quad (\text{Eqn.1})$$

Where, e = elementary charge

$E^{\circ}(D^{+}/D)$ = the first oxidation potential of ZnPc-cytidine **2** = 0.49 V (vs. Ag/AgNO₃)

$E^{\circ}(A/A^{\cdot})$ = the first reduction potential of guanosine-C₆₀ **3** = -0.85 V (vs. Ag/AgNO₃)

E_{00} = The energy of the lowest excited singlet state of the ZnPc-cytidine **2**

(E_{00} was calculated from the intersection of the normalized absorption and emission spectra of **2**, resulting in a wavelength of 695 nm)

$$E = hc/\lambda. \text{ Therefore, } E = (6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.997 \times 10^8 \text{ m}\cdot\text{s}) / 695 \times 10^{-9} \text{ m} = 2.856 \times 10^{-19} \text{ J}$$

$$\text{Since } 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$2.856 \times 10^{-19} \text{ J} = 1.78 \text{ eV}$$

Substituting the values of $E^{\circ}(D^{+}/D)$, $E^{\circ}(A/A^{\cdot})$, and E_{00} into Eqn.1:

$$\Delta G_{CS}^{\circ}/eV = [0.49 - (-0.85)] - 1.78 = -0.44 \text{ eV}$$

$$\text{Estimation of } \Delta G_{CR}^{\circ} = - [E^{\circ}(D^{+}/D) - E^{\circ}(A/A^{\cdot})] = - (0.49 - (-0.85)) = -1.34 \text{ eV}$$

Iib. Photophysical Studies

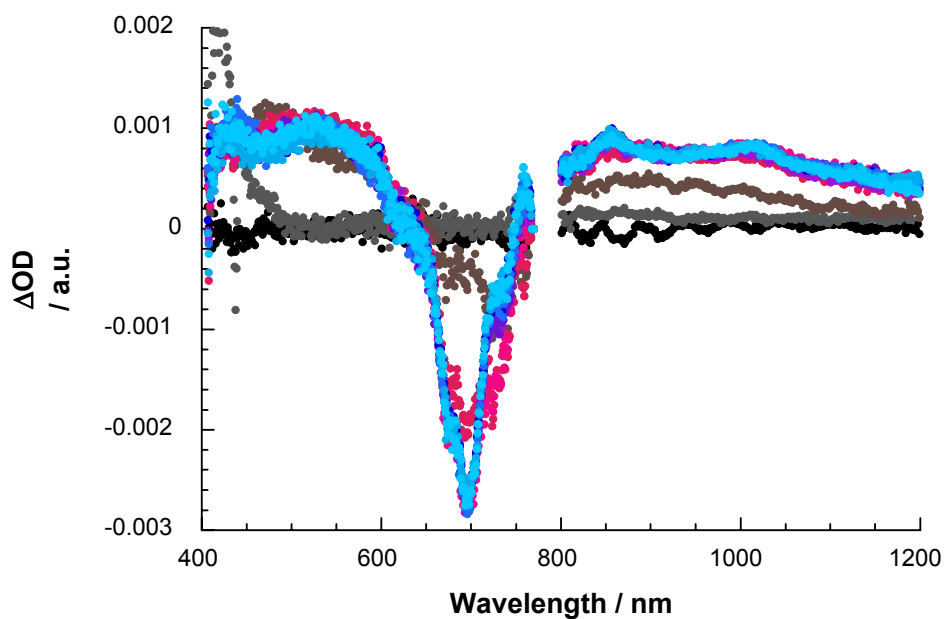


Fig. S2 Differential absorption spectra (visible and near infrared) obtained upon femtosecond flash photolysis (387 nm) of ZnPc-C (1.3×10^{-5} M) and G-C₆₀ (5.1×10^{-5} M) in nitrogen saturated toluene / dichloromethane solutions (4:1 v/v) with several time delays between 0 and 20 ps at room temperature.

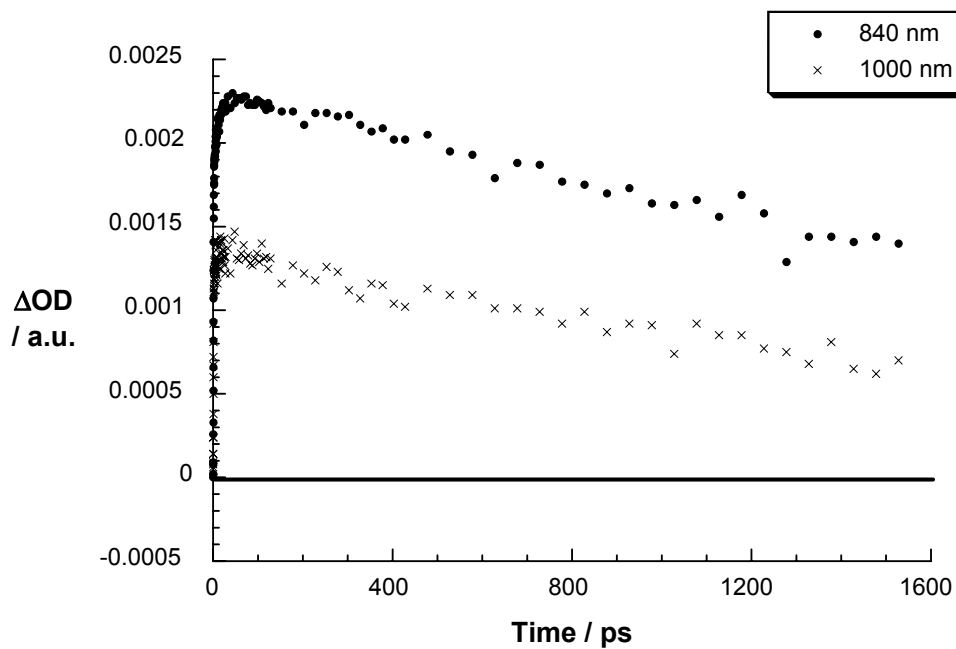


Figure S3: Time-absorption profiles of the spectra shown in Figure 4 at 840 nm (circles) and 1000 nm (crosses), monitoring the formation and decay of the radical ion pair state.