Supplementary Material (ESI) for Chemical Communications

Synthesis and photophysics of a porphyrin-fullerene dyad assembled through Watson-Crick hydrogen bonding

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Supporting Information

I. Synthetic Experimental

4-Amino-5-[(5''-ethynylphenyl)-10'',15'',20''-triphenylporphinatoZn(II)]-1-[2',3',5'-tri-*O*-(*tert*-butyl-dimethylsilyl)-ß-D-ribofuranosidyl]-pyrimidin-4-one (1):

Porphyrin **3**[1] (0.06 g, 0.09 mmol) and iodocytidine (0.1 g, 0.14 mmol) **4**[2] were added to a mixture of dry toluene/triethylamine (2:1) (6 ml) under an argon atmosphere. The resulting solution was bubbled with argon for 20 min. At this point, CuI (0.08 g, 0.04 mmol) and $Pd(PPh_3)_4$ (0.02 g, 0.02 mmol) were added. The reaction mixture was then stirred and heated at 50 ºC for 12 hr. Subsequently, the solvents were removed in vacuo and the crude material was purified using column chromatography on a silica gel column using ethylacetate/hexanes (2/3) as the eluent. A second silica gel column using the same eluent system, was performed to provide **1** in the form of a purple solid. (7.7×10^{-3} g, 67 % yield). M.P. 210 ºC (decomp); UV/Vis (CH_2Cl_2) λ_{max} [nm] (ε in M^{-1} cm^{-1}): 420 (4.9×10^5), 548 (2.0×10^4), 578 (5.0×10^3); ^{1}H NMR (500 MHz, CD_2Cl_2 with a drop of CD_3OD) δ 8.92-8.85 (m, 8 H), 8.41 (s, 1 H), 8.25 (d, *J* = 8.5 Hz, 2 H), 8.23-8.21 (m, 6 H), 7.90 (*J* = 8.5 Hz, 2 H), 7.78-7.74 (m, 9 H), 5.98 (d, *J* = 4.0 Hz, 1 H), 4.24 (t, *J* = 3.5 Hz, 1 H), 4.16 (m, 2 H), 4.12 (d, *J* = 11.0 Hz, 1 H), 3.87 (d, *J* = 11.0 Hz, 1 H), 1.08 (s, 9 H), 0.95 (s, 9 H), 0.94 (s, 9 H), 0.32 (s, 6 H), 0.17 (s, 3 H), 0.144 (s, 3 H), 0.137 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (125 MHz, CD_2Cl_2 with a drop of MeOD) δ 163.8, 154.2, 149.5, 149.43, 149.35, 148.9, 143.5, 143.2, 142.5, 133.9, 133.8, 131.1, 131.00, 130.95, 130.5, 128.9, 126.6, 125.7, 120.5, 120.3, 120.1, 118.7, 95.0, 90.7, 89.0, 83.9, 80.3, 76.0, 70.2, 61.3, 28.9, 25.4, 24.9, 17.9, 17.3, 17.2, -5.2, -5.5, -5.8, -5.87, -5.93, -6.2; HR-MS (CI): *m/z* 1284.4961 $[M+ H]^+$, calcd for $C_{73}H_{81}N_7O_5Si_3Zn$: 1284.4977; calcd for

$C_{73}H_{81}N_7O_5Si_3Zn{\cdot}MeOH{\cdot}CH_2Cl_2$: C 64.20, H 6.25, N 6.99; found C 64.33, H 6.73, N 6.36.

8-Formyl-2-isobutyramido-9-[2′,3′,5′-tri-*O*-(*tert*-butyldimethylsilyl)-ß-D-ribofuranosidyl]-purin-6-one (6):

Nucleoside **5**[3] (1.25 g, 1.73 mmol), dissolved in 90 ml of dry dichloromethane, was treated with ozone at -78 ºC for 3 hr. The solution was purged with argon, followed by the addition of methyl sulfide (0.16 ml, 2.25 mmol). The reaction was left to stir for 12 hr while warming to room temperature. Subsequently, the solvent was removed in vacuo and the resulting crude mixture was purified by column chromatography on a silica gel column using ethylacetate/hexanes (1/1) as the eluent. This yielded the formyl derivative **6** in the form of a white powder (0.6 g, 52 % yield). M.P. 190 ºC (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.2 (s, 1 H), 9.82 (s, 1 H), 8.64 (s, 1 H), 6.52 (d, *J* = 6.4 Hz, 1 H), 4.96 (m, 1 H), 4.39 (t, *J* = 2.4 Hz, 1 H), 3.98-3.92 (m, 2 H), 3.69 (m, 1 H) 2.67 (m, 1 H), 1.23 (d, *J* = 6.8 Hz, 3 H), 1.19 (d, *J* = 6.8, Hz, 3 H), 0.91 (s, 9 H), 0.82 (s, 9 H), 0.70 (s, 9 H), 0.12 (s, 3 H), 0.10 (s, 3 H), 0.01 (s, 3 H), -0.03 (s, 3 H), -0.13 (s, 3 H), -0.40 (s, 3 H)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.2, 178.7, 155.5, 150.8, 148.9, 144.3, 123.0, 88.0, 85.7, 72.9, 72.1, 62.5, 36.5, 25.8, 25.5, 19.0, 18.6, 18.3, 18.0, 17.7, -4.4, -4.5, -4.6, -5.2, -5.4, -5.5; HR-MS (FAB): *m/z* 724.3969 $[M+H]^+$, calcd for $C_{33}H_{61}N_5O_7Si_3$: 724.3957; calcd for $C_{33}H_{61}N_5O_7Si_3$: C 54.74, H 8.49, N 9.67; found C 54.94, H 8.50, N 9.48.

8-{2″-(1″-methyl-3″,4″[C60]fulleropyrrolidinyl)}-2-isobutyramido-9-[2′,3′,5′-tri-*O*-(*tert*-butyldimethylsilyl)-ß-D-ribofuranosidyl]-purin-6-one (7):

A mixture of nucleoside **6** (0.246 g, 0.34 mmol), C_{60} (0.245 g, 0.34 mmol) and N-methylglycine (0.151 g, 1.7 mmol) in dry toluene (150 ml) was heated to reflux under an argon atmosphere for 24h. After cooling, the solution was evaporated and the residue purified by column chromatography on a silica gel column using toluene and toluene/ ethylacetate (4/1) as the eluents. The resulting product was triturated with methanol, filtered, and washed with methanol and with hexanes, yielding **7** as a dark brown solid (0.14 g, 28%). M.P. 250 ºC (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.93 (s, 1 H), 7.57 (s, 1 H), 7.48 (d, J = 8.1 Hz, 1 H), 5.73 (s, 1 H), 5.47 (dd, $J' = J''$= 4.1 Hz, 1H), 4.93 (d, J = 9.4 Hz 1 H), 4.35 (d, J = 4.1 Hz, 1 H), 4.22 (d, J = 9.4 Hz, 1H), 3.98-3.90 (m, 1 H), 3.75-3.60 (m, 2 H), 2.91 (s, 3H), 2.60-2.45 (m, 1 H), 1.29–1.22 (m, 6 H), 1.01 (s, 9 H), 0.92 (s, 9 H), 0.84 (s, 9 H), 0.17 (s, 3 H), 0.16 (s, 3 H), 0.09 (s, 3 H), 0.07 (s, 3 H), -0.02 (s, 3 H), -0.05 (s, 3 H)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 155.4, 155.2, 153.9, 153.4, 151.3, 149.6, 147.4, 147.3, 146.9, 146.6, 146.5, 146.4, 146.3, 146.2, 146.1, 146.0, 145.9, 145.8, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.1, 145.0, 144.9, 144.7, 144.6, 144.5, 144.3, 143.1, 143.0, 142.6, 142.5, 142.4, 142.3, 142.2, 142.1, 142.0, 141.9, 141.8, 141.7, 141.6, 141.5, 141.4, 140.3, 140.0, 139.8, 138.3, 136.7, 136.0, 122.3, 86.1, 84.4, 75.7, 72.4, 71.7, 69.2, 63.3, 39.9, 36.8, 26.1, 26.0, 25.9, 19.0, 18.9, 18.5, 18.1, -3.4, -4.3, -4.4, -5.2, -5.4; ES-MS : *m/z* 1471 $[M+H]^+$, UV/Vis (CH_2Cl_2) λ_{max} [nm] (ε in M^{-1} cm^{-1}): 257 (6.3×10^4), 320 (sh), 431 (20).

8-{2″-(1″-methyl-3″,4″[C60]fulleropyrrolidinyl)}-2-amino-9-[2′,3′,5′-tri-*O*-(*tert*-butyldimethylsilyl)-ß-D-ribofuranosidyl]-purin-6-one (2):

Fulleropyrrolidine-nucleoside **6** (0.147 g, 0.1 mmol) was treated with an ammonia saturated solution of dichloromethane/methanol (3/1) and allowed to stir at room temperature. During this time, the reaction was monitored by TLC analysis. When the reaction was deemed complete (ca. 24 h), the solvent was removed and the residue was triturated with hexanes. It was then filtered and the precipitate collected in this way was washed with hexanes. The crude product was extracted in a soxhlet apparatus with dichloromethane for 24 h, yielding **2** as a dark brown solid (0.09 g, 65%). M.P. 250 ºC (decomp); ^{1}H NMR (500 MHz, $CDCl_3$ with a drop of CD_3OD) δ 12.45 (brs, 1 H), 5.70 (dd, *J’* = *J’’*= 4.1 Hz, 1H), 5.52 (s, 1 H), 4.88 (d, *J* = 9.4 Hz 1 H), 4.51 (d, *J* = 4.1 Hz, 1 H), 4.31 (d, *J* = 9.4 Hz, 1H), 4.00-3.90 (m, 1 H), 3.75-3.65 (m, 2 H), 3.60-3.50 (m, 2 H), 2.85 (s, 3H), 0.98 (s, 9 H), 0.89 (s, 9 H), 0.83 (s, 9 H), 0.09 (s, 6 H), 0.03 (s, 3 H), 0.01 (s, 3 H), -0.07 (s, 3 H), -0.12 (s, 3 H)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 153.0, 152.8, 149.6, 149.0, 148.4, 147.9, 147.6, 147.3, 146.4, 146.2, 146.0, 145.8, 145.5, 145.3, 144.7, 144.5, 144.3, 143.1, 143.0, 142.6, 142.1, 141.7, 140.3, 140.0, 135.8, 122.3, 85.9, 84.2, 75.8, 74.0, 72.3, 69.5, 69.2, 63.9, 40.2, 26.1, 26.0, 25.7, 25.3, 18.9, 18.3, 18.1, -3.6, -4.4, -5.0; ES-MS : *m/z* 1401 $[M+H]^+$, UV/Vis (CH_2Cl_2) λ_{max} [nm] (ε in M^{-1} cm^{-1}): 256 (6.0 x 10^4), 320 (sh), 430 (20).

II. Electrochemical Analysis.

A single-compartment, three electrode, glass electrochemical cell was employed for the cyclic voltammetric studies. Platinum mesh (Aldrich) and silver wire (Alfa Aesar) were used as the counter and quasi-reference electrodes, respectively, while a gold disk UME (r = 12.5 μm) was used as the working electrode. Measurements were performed with a CH Instruments 700A potentiostat. All electrochemical studies were taken with a quiescent solution and at room temperature (23 ± 2° C). Prior to reductive measurements, the solution was purged with N_2 for several minutes. Electrolyte solutions were prepared using recrystallized tetrabutylammonium hexafluorophosphate (Aldrich) and A.C.S spectranalyzed dichloromethane (Fisher). Following each measurement, ferrocene ($FeCp_2$) was added ($[FeCp_2] \sim 1mM$) and all potentials were referenced to the potential for the ferrocene/ferrocenium couple. All scans were recorded at 20 mV s^{-1}.

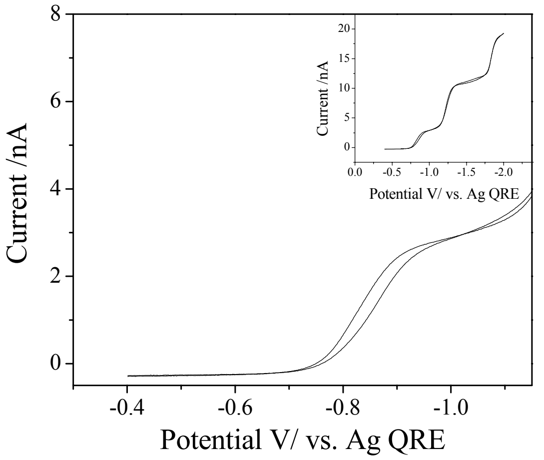


Figure 1. Room temperature cyclic voltammogram of **2** (~1 mM) in CH_2Cl_2 with (n-Bu_4N)PF_6 (0.1 M). Inset depicts multiple further reductions at more negative applied potentials. From these studies, an E^0 of -1.082 V vs. Fc/Fc^+ was calculated for **2**.

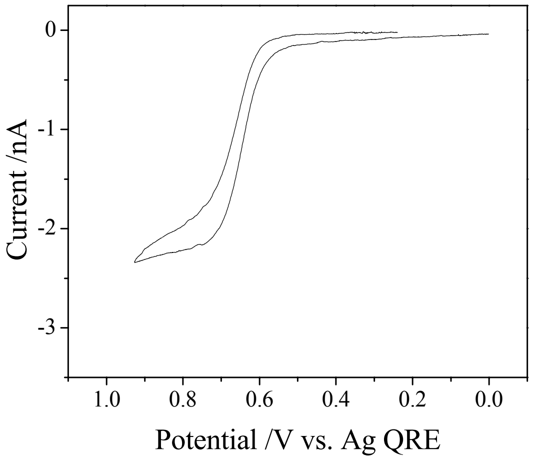


Figure 2. Room temperature cyclic voltammogram of **1** (~1 mM) in CH_2Cl_2 with (n-$Bu_4N)PF_6$ (0.1 M). From these studies, an E^0 of 0.317 V vs. Fc/Fc^+ was calculated for **1**.

IIIa. Estimation of Driving Force

Estimation of ΔG^o_{ET}

$$\Delta G_{CS}{}^o/eV = e[E^o(D^{+\bullet}/D) - E^o(A/A^{-\bullet})] - E_{00} \qquad \text{(Eqn.1)}$$[4]

Where, e = elementary charge

$E^o(D^{+\bullet}/D)$ = the first oxidation potential of Zn-porphyrin-cytidine **1**
= **0.317 V** (vs. ferrocene in CH_2Cl_2)

$E^o(A/A^{-\bullet})$ = the first reduction potential of guanosine-C_{60} **2**
= **-1.082 V** (vs. ferrocene in CH_2Cl_2)

E_{00} = The energy of the lowest excited singlet state of the Zn-porphyrin-cytidine **1**

(E_{00} was calculated from the intersection of the normalized absorption and emission spectra of **1**, resulting in a wavelength of 560 nm)

$E = hc/\lambda$. Therefore, $E = (6.626 \times 10^{-34}\ \mathrm{J{\bullet}s})(2.997 \times 10^{8}\mathrm{m{\bullet}s}) / 560 \times 10^{-9}\mathrm{m}$

$= 3.546 \times 10^{-19}$ J

Since 1 eV = 1.602×10^{-19} J

3.546×10^{-19} J = **2.21 eV**

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

$\boldsymbol{\Delta G^{o}_{\mathrm{ET}}/\mathrm{eV}} = [0.317 - (-1.082)] - 2.21 = \mathbf{-0.81\ eV}$

Estimation of $\boldsymbol{\Delta G_{\mathrm{CR}}{}^{o} = -\,[E^{o}(\mathrm{D}^{+\bullet}/\mathrm{D}) - E^{o}(\mathrm{A}/\mathrm{A}^{-\bullet})]}$
$= -\,(0.317 - (-1.082))$
$\mathbf{= -1.4\ eV}$

IIIb. Estimation of k_{cs}, ϕ and K_a

The rate constant for the forward electron transfer (k_{cs}) can be estimated from Eqn. 2, where τ_1 (2.1 ns) is the lifetime for the longer lived component and τ_2 (0.6 ns) is the lifetime of the shorter lived component.

$k_{cs} = (1/\tau_2) - (1/\tau_1)$ Eqn. 2

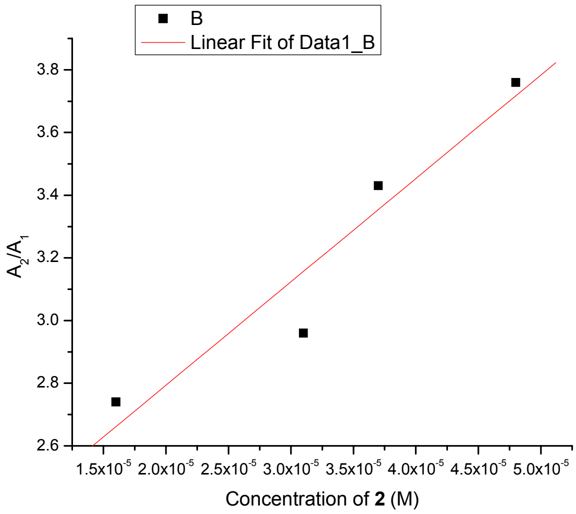
$= 1.2 \times 10^{9}\ \mathrm{s}^{-1}$

The corresponding quantum efficiency is 0.71 ($\phi = \tau_2\, k_{cs}$)

On the assumption that the fractional amplitudes (A_2 and A_1) are proportional to the concentration of each emitting species is true, it is possible to calculate the binding constant (K_a) of the H-bonded dyad **I** from Eqn. 3.

$K_a = A_2/A_1[Q]$ Eq.3

A plot of A_2/A_1 versus [Q] (the concentration of the quencher **2**) yielded a value for the association constant, K_a (ca. $3.3 \times 10^{4}\ \mathrm{M}^{-1}$).



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[1/20/2005 13:46 "/Graph1" (2453390)]
Linear Regression for Data1_B:
Y = A + B * X

Parameter        Value   Error
------------------------------------------------------------
A        2.13362         0.24463
B        32996.25468     6996.58775
------------------------------------------------------------

R        SD        N        P
------------------------------------------------------------
0.95786         0.16168         4         0.04214
------------------------------------------------------------
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