Supporting Information for

Strong Electronic Coupling and Electron Transfer in a $Ce_2@I_h$-C_{80}–H_2P Electron Donor Acceptor Conjugate

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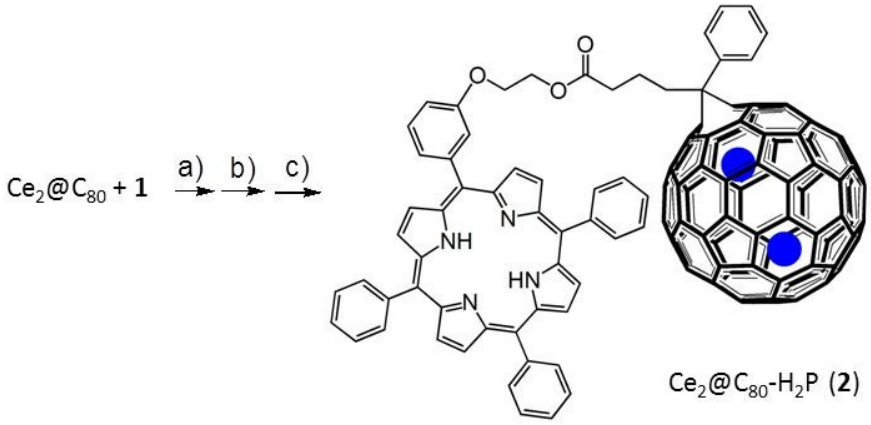
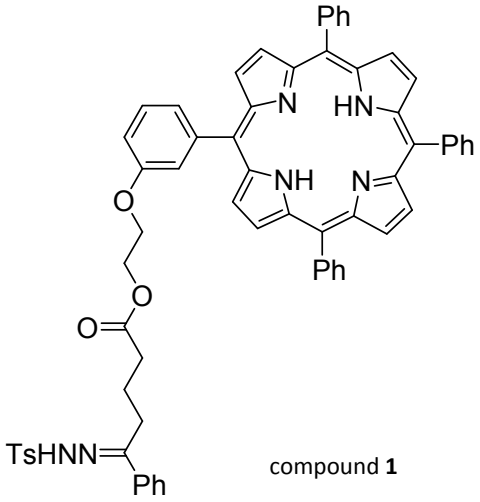


Scheme S1. Synthesis of $Ce_2@C_{80}$-H_2P. a) NaOMe, o-DCB, MeCN, 75°C, Ar; b) $CHCl_2COOH/CS_2$/acetone, rt.; c) washing by $NaHCO_3/H_2O$ and extracted by toluene.



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Scheme S2. Schematic structure of compound **1** synthesized using the previously reported method.[1]

Reference.

1. D. M. Guldi, L. Feng, S. G. Radhakrishnan, H. Nikawa, M. Yamada, N. Mizorogi, T. Tsuchiya, T. Akasaka, S. Nagase, M. Ángeles Herranz and N. Martín, *J. Am. Chem. Soc.*, 2010, 132, 9078-9086.)

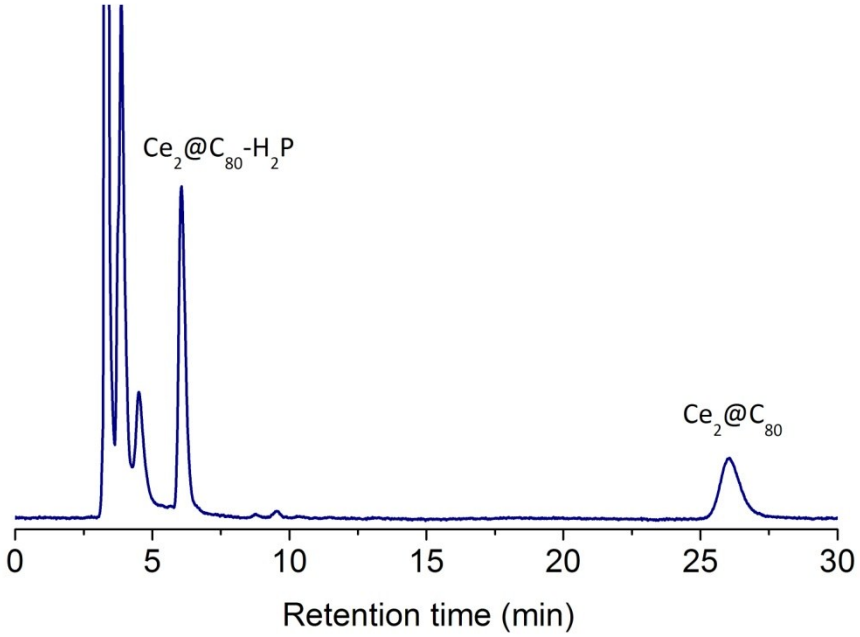

Figure S1: HPLC profile of the reaction mixture of $Ce_2@C_{80}$ and **1** on 5PYE column using toluene as elute and with a flow rate of 1 mL/min.

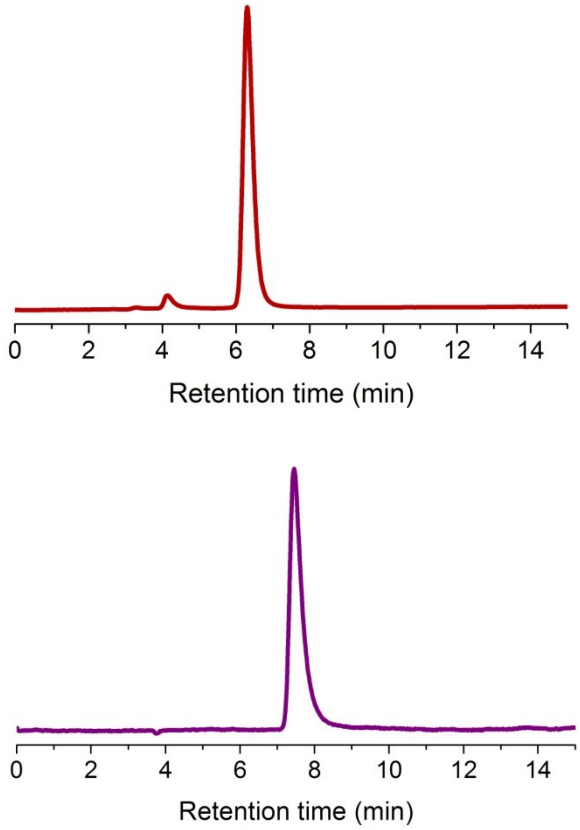

Figure S2: HPLC profile of isolated $Ce_2@C_{80}$-H_2P on a Buckyclutcher column (up), in comparison with that of the previously reported $Ce_2@C_{80}$-ZnP on the same column (down) using toluene as elute and with a flow rate of 1 mL/min, showing their different retention times.

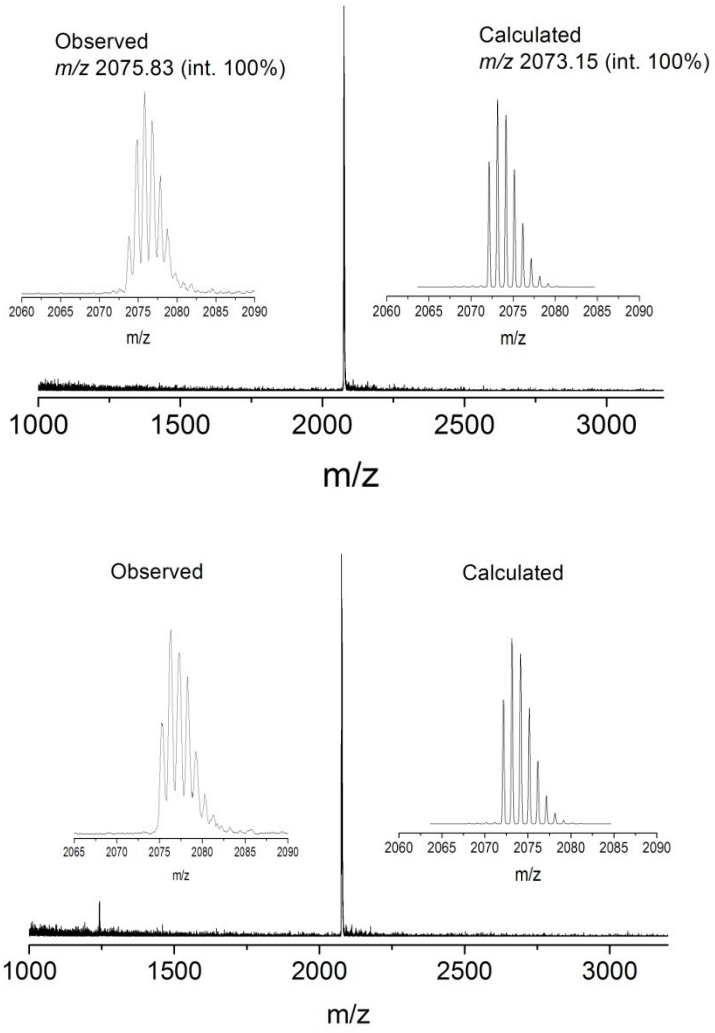

Figure S3: MALDI-TOF mass spectra of $Ce_2@C_{80}$-H_2P in positive (up) and negative (down) mode.

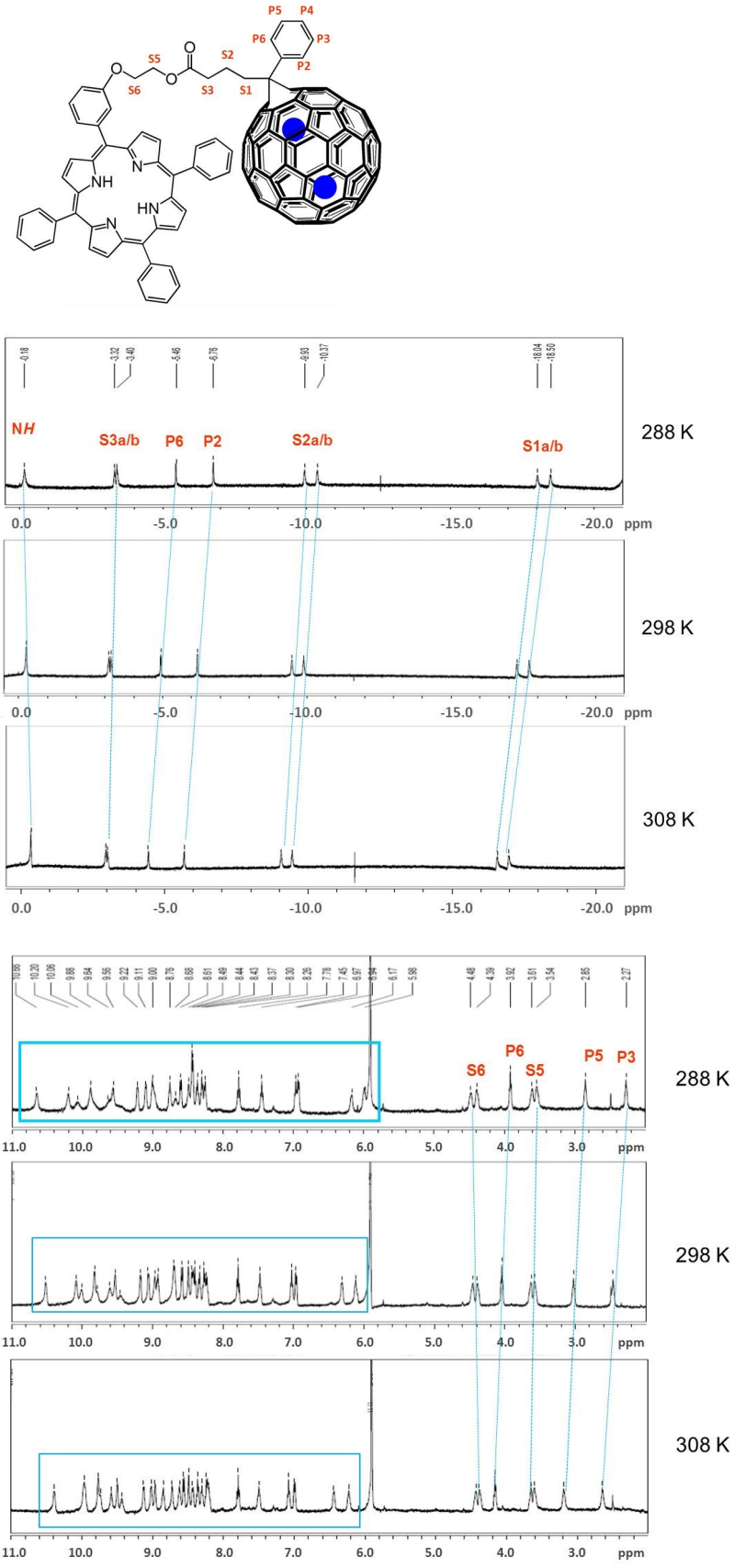

Figure S4: VT-^{1}H NMR (500 MHz, $C_2D_2Cl_4$) of the conjugate $Ce_2@C_{80}$-H_2P.

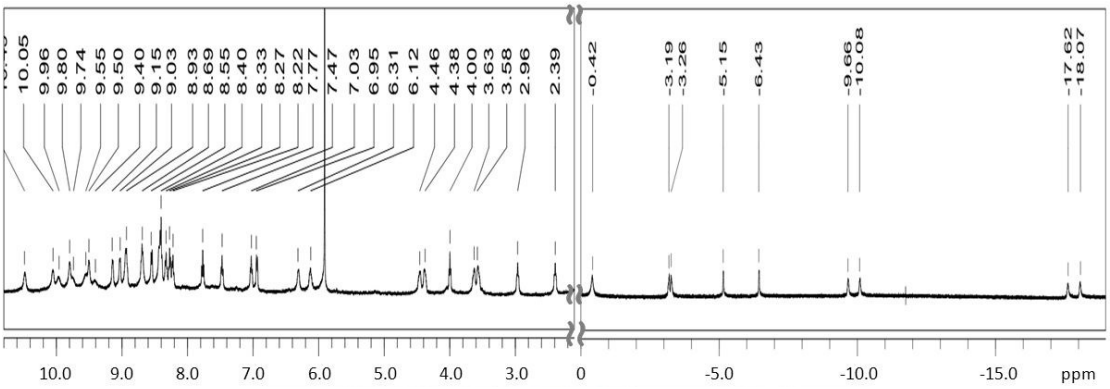

Figure S5: ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) of the conjugate $Ce_2@C_{80}$-H_2P at 293 K.

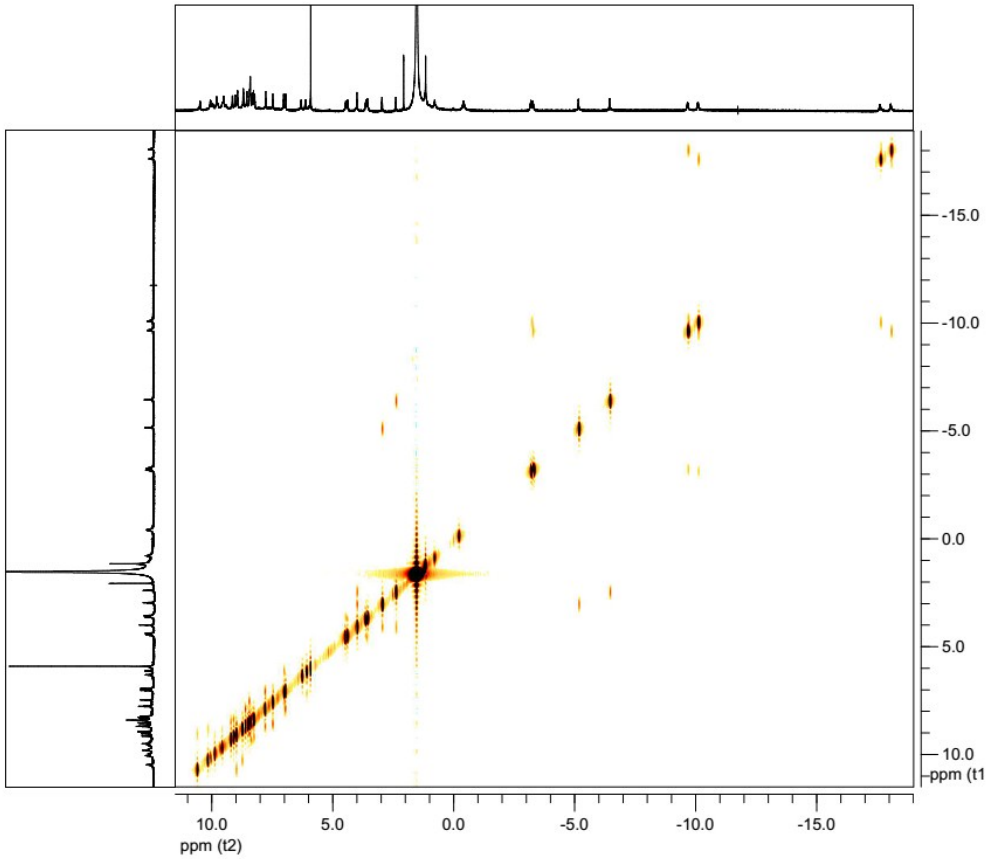

Figure S6: ^{1}H-^{1}H Cosy (500 MHz, $C_2D_2Cl_4$) of the conjugate $Ce_2@C_{80}$-H_2P at 293 K.

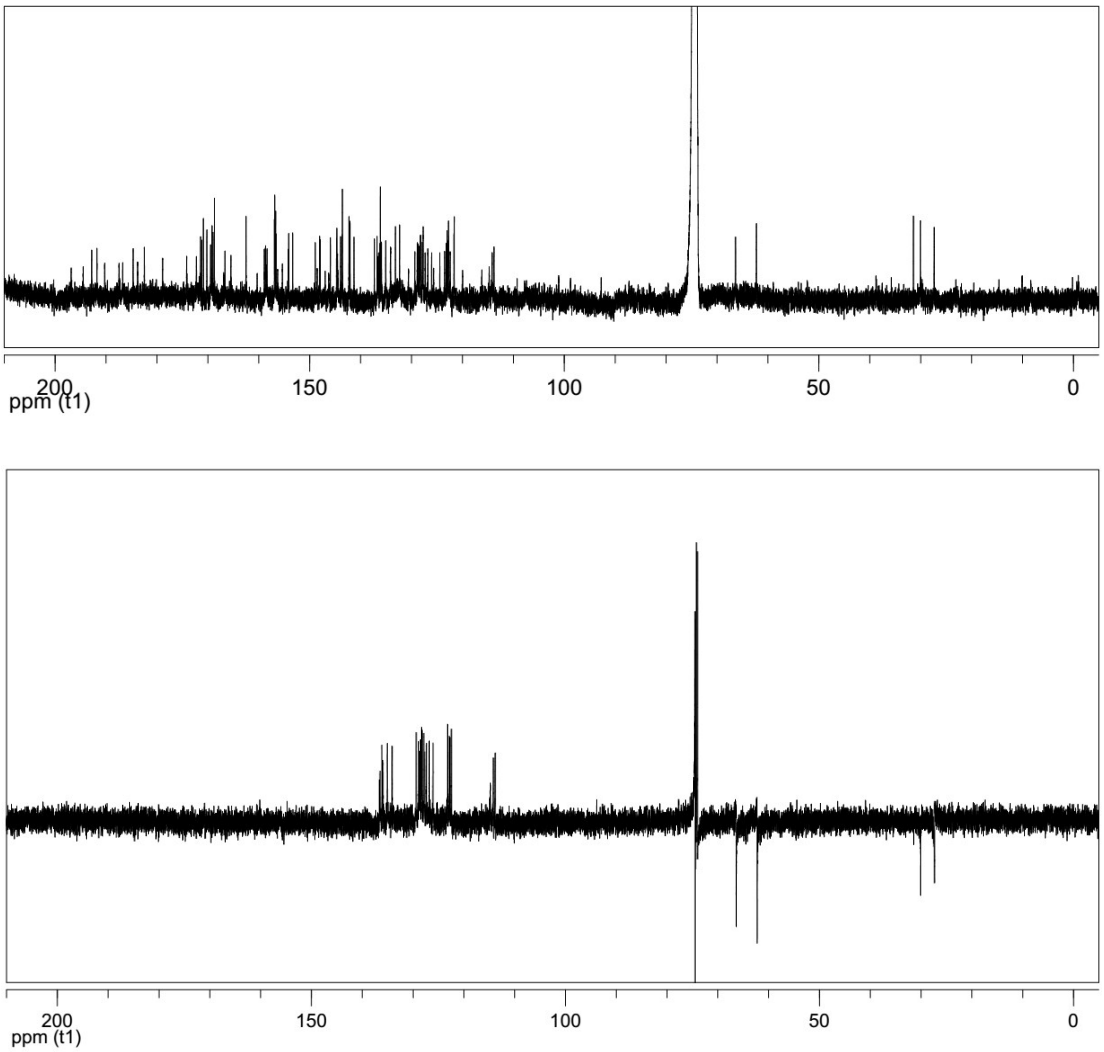

Figure S7: ^{13}C NMR (125 MHz, $CDCl_3$) (up) and DEPT135 (down) of the conjugate $Ce_2@C_{80}$-H_2P at 293 K.

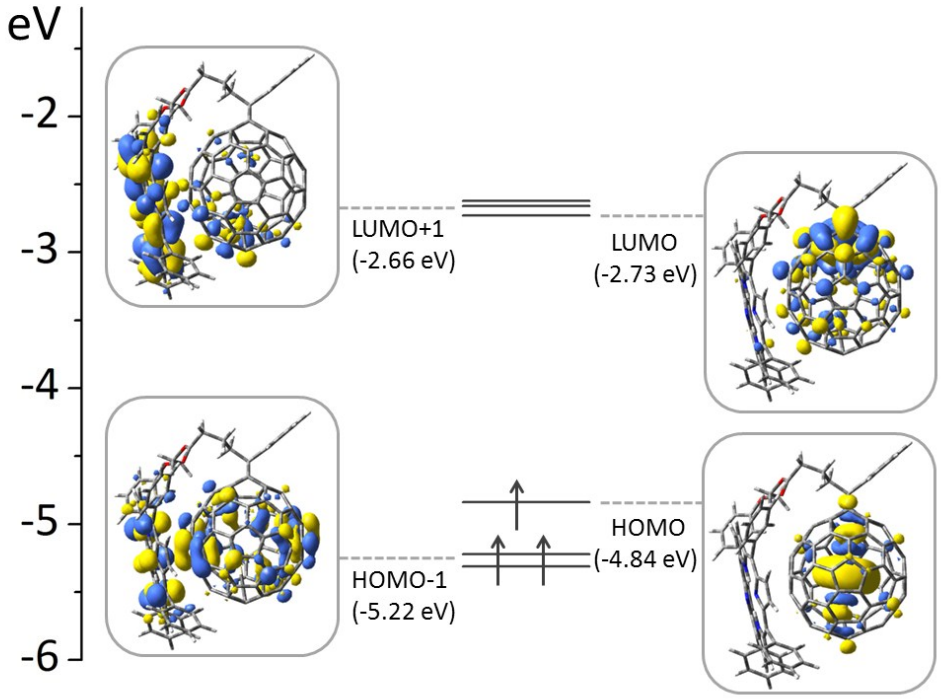

Figure S8: MO diagram of **2**. Only the terms for alpha electrons are shown.

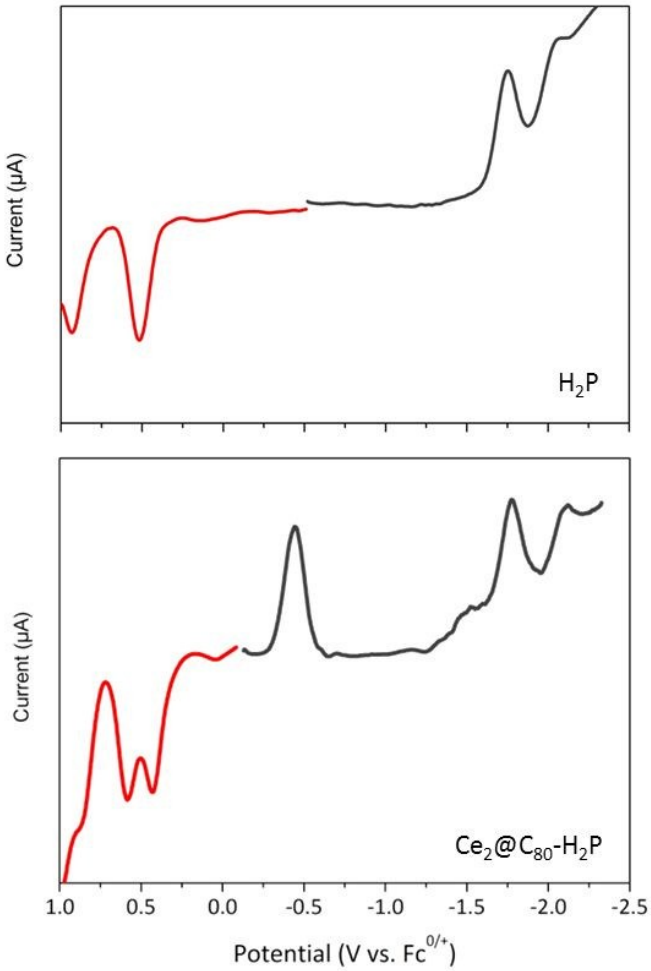

Figure S9: Differential pulse voltammograms of H_2P (up) and conjugate $Ce_2@C_{80}$-H_2P (down) in *o*-dichlorobenzene (supporting electrolyte: 0.05 M (*n*-Bu)$_4$NPF$_6$; scan rate: 20mVs^{-1}).

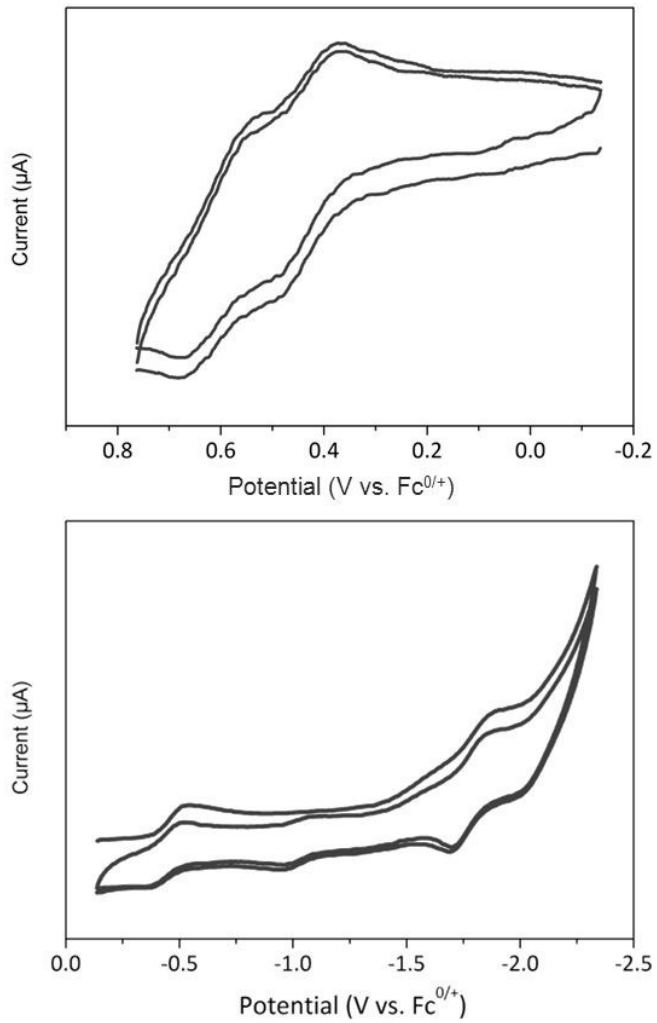

Figure S10: Cyclic voltammograms of conjugate $Ce_2@C_{80}$-H_2P; a) oxidation steps and b) reduction steps in *o*-dichlorobenzene (supporting electrolyte: 0.05 M $(n\text{-Bu})_4NPF_6$; scan rate: 100mVs^{-1}).

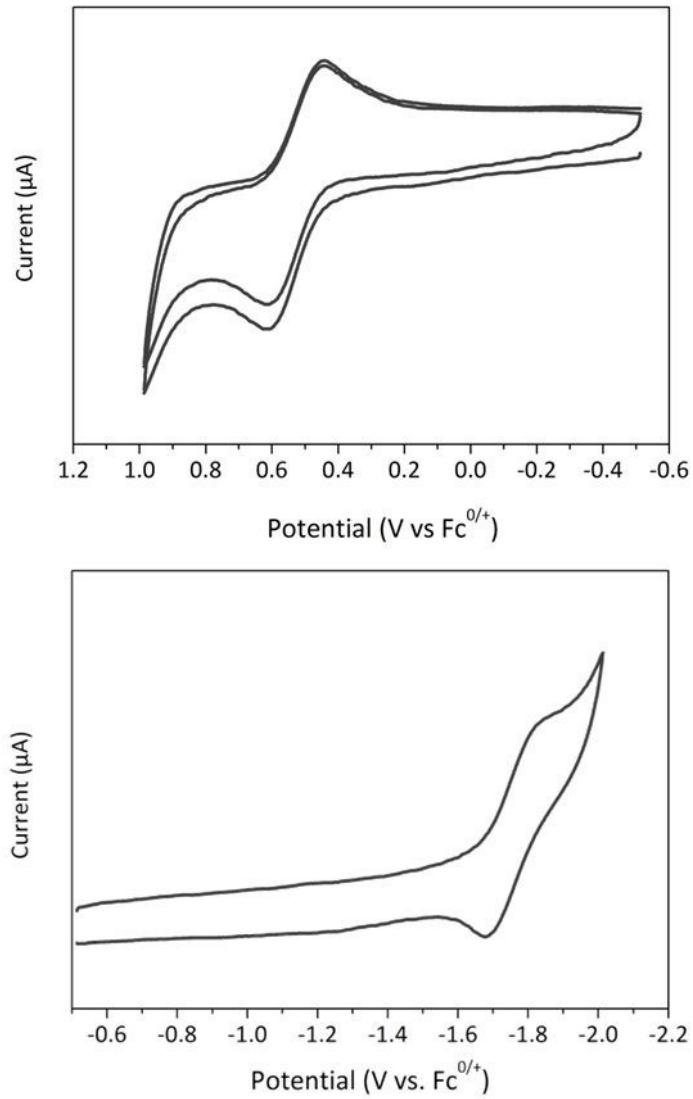

Figure S11: Cyclic voltammograms of conjugate H_2P; a) oxidation step and b) reduction step in *o*-dichlorobenzene (supporting electrolyte: 0.05 M (*n*-Bu)$_4$NPF$_6$; scan rate: 100mVs^{-1}).

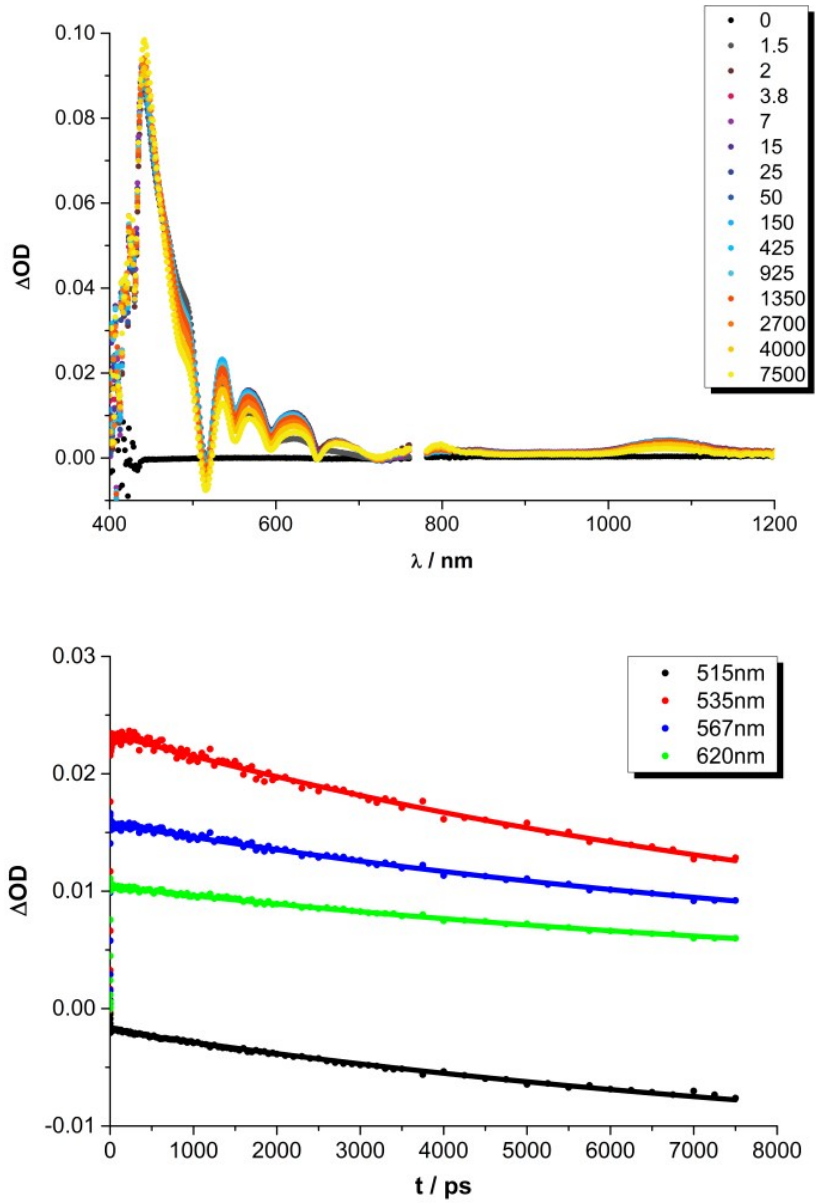

Figure S12: (Top) Differential absorption spectra (visible and near infrared) obtained upon femtosecond flash photolysis (420 nm) of H_2P (10^{-5} M) in argon-saturated THF with several time delays between 0 and 7500 ps at room temperature. (Bottom) Time-absorption profiles of the spectra shown above at 515, 535, 567, and 620 monitoring the intrinsic intersystem crossing.