

**Supplementary Materials for  
Molecular-Scale Engineering of the Charge-Transfer Excited States in Non-Covalently Bound  
Zn-Porphyrin and Carbon Fullerene based Donor-Acceptor Complex**

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**Table S1:** Correspondence between HOMO and IP, and LUMO and EA calculated using OT-RSH/6-31G (d) for all monomers (PCBM, ZnPor, ZnChl and ZnBChl) and three D-A complexes (ZnPor@PCBM, ZnChl@PCBM and ZnBChl@PCBM). Electronic HOMO-LUMO gaps ( $\Delta E_{H-L}$ ) calculated using OT-RSH and B3LYP are also provided for comparison. All energies are in eV.

Systems	HOMO	IP ( $\Delta$ SCF)	LUMO	EA ( $\Delta$ SCF)	$\Delta E_{H-L}$	
					B3LYP	OT-RSH
PCBM	-7.3	-7.3	-2.0	-2.0	2.6	5.3
ZnPor	-6.6	-6.6	-1.0	-1.0	3.1	5.6
ZnChl	-6.2	-6.2	-1.0	-1.0	2.7	5.2
ZnBChl	-5.6	-5.6	-1.1	-1.1	2.1	4.5
ZnPor@PCBM	-6.3	-6.3	-2.0	-2.0	2.1	4.3
ZnChl@PCBM	-6.0	-6.0	-2.0	-2.0	1.7	4.0
ZnBChl@PCBM	-5.4	-5.4	-2.0	-2.0	1.2	3.4

**Table S2:** Low-lying Q-band, B-band and CT excited-electronic states for all monomers and three D-A complexes calculated in the gas-phase using TDDFT/OT-RSH. All energies are in eV. Oscillator strengths are listed within bracket. H and L stand for HOMO and LUMO, respectively. LE and CT indicate local and charge-transfer excitation, respectively. Percentage of significant MO configuration state function (CSF) for each excited-state is also provided.

System	Excitation Energy	Important FMO Contribution (%)	Nature of Electronic State
PCBM	2.3(0.0020)	H→L(92)	LE
	2.4(0.0000)	H→L+1(82)	LE
	2.4(0.0000)	H-2→L(69)	LE
	2.4(0.0000)	H-1→L(71)	LE

ZnPor	2.4 (0.0038)	H→L(36) H-1→L+1(33)	LE (Q)
	2.4 (0.0038)	H-1→L(33); H→L+1(36)	LE (Q)
	3.5 (0.0001)	H-2→L(99)	LE
	3.5 (0.0001)	H-2→L+1(99)	LE
	3.7(1.0126)	H-1→L+1(48); H→L(47)	LE (B)
	3.7 (1.0131)	H→L+1(47); H-1→L(48)	LE (B)
ZnChl	2.3(0.1294)	H→L(81)	LE(Q)
	2.6(0.0014)	H-1→L(57); H→L+1(41)	LE
	3.5(0.0003)	H-2→L(98)	LE
	3.7(0.9908)	H→L+1(57); H-1→L(39)	LE(B)
ZnBChl	1.9(0.2740)	H→L(94)	LE(Q)
	2.5(0.0411)	H-1→L(71); H→L+1(28)	LE
	3.4(0.0002)	H-3→L(99)	LE
	3.6(0.0000)	H-2→L(97)	LE
	3.9(0.8161)	H→L+1(64)	LE(B)
	4.0(0.2523)	H-4→L(81)	LE
ZnPor@PCBM	2.1(0.0005)	H→L(34); H→L+1(32); H-2→L(18)	Partial CT [LE(A)+CT]
	2.2(0.0015)	H-2→L(37); H→L+1(31)	Partial CT [LE(A)+CT]
	2.3(0.0007)	H→L+2(9); H-1→L(14); H-2→L(20) H-4→L(10)	Partial CT [LE(A)+CT]
	2.3(0.0002)	H-1→L+1(33); H-2→L+1(24)	Partial CT [LE(A)+CT]
	2.3(0.0002)	H-1→L(14); H-2→L+1(18) H-3→L(44)	Partial CT [LE(A)+CT]
	2.3(0.0003)	H→L+2(22); H-4→L(42)	Partial CT [LE(A)+CT]
	2.3(0.0001)	H-1→L+1(17); H-2→L+1(24) H-3→L(30)	Partial CT [LE(A)+CT]
	2.4(0.0020)	H→L(16); H→L+2(37); H-4→L(13)	Partial CT [LE(A)+CT]
	2.4(0.0010)	H-1→L+2(19); H-1→L+3(13)	Q+CT

		H-1 → L+4(13)	
	2.4(0.0004)	H → L+3(5); H → L+4(31); H-1 → L+3(27)	Q
	3.4(0.1625)	H → L+4(15); H-1 → L+3(16)	B
	3.4(0.2334)	H → L+3(11); H → L+4(13); H-1 → L+3(15); H-1 → L+4(11)	B
ZnChl@PCBM	1.9 (0.0007)	H → L (38); H → L+1 (53); H → L+5 (5)	CT
	2.0 (0.0004)	H → L (37); H → L+1 (31); H → L+2 (26)	CT
	2.1 (0.0020)	H → L (11); H → L+2 (39) H-1 → L (13); H-1 → L+1 (17)	CT
	2.1 (0.0008)	H → L (8); H → L+2 (27); H-1 → L (17) H-1 → L+1 (24); H-2 → L (9)	CT
	2.2 (0.0023)	H-1 → L+1 (26) H-2 → L(40)	Partial CT [LE (A) + CT]
	2.3 (0.0008)	H-1 → L (19); H-1 → L+2 (23) H-2 → L (28)	Partial CT [LE (A) + CT]
	2.3 (0.0042)	H-2 → L+1 (46); H-3 → L (23)	LE (A)
	2.3 (0.0532)	H → L+3 (50); H-1 → L+2 (10) H-1 → L+6 (10); H-2 → L+1 (10)	Q
	3.5 (0.1958)	H → L+6 (35); H-1 → L+3 (14)	CT + B
ZnBChl@PCBM	1.3 (0.0006)	H → L (33); H → L+1 (60); H → L+5 (5)	CT
	1.4 (0.0002)	H → L (48); H → L+1 (26) H → L+2 (22)	Partial CT [L.E (D) + CT]
	1.5 (0.0005)	H → L (17); H → L+1 (8) H → L+2 (71)	Partial CT [L.E (D) + CT]
	2.0 (0.1497)	H → L+3 (81)	Q
	3.9 (0.0842)	H-9 → L+3 (14); H → L+9 (8)	CT + B

**Table S3:** Gas-phase exciton binding ( $E_{xb}$ ) energies for the lowest-excited CT state ( $CT_1$ ) for all three D-A complexes calculated using B3LYP and OT-RSH functionals.

D-A Complex	$E_{xb}$ (eV)	
	B3LYP	OT-RSH
ZnPor@PCBM	0.4	2.2
ZnChl@PCBM	0.4	2.1
ZnBChl@PCBM	0.4	2.1

**Table S4:** Comparison of gas-phase excited-state energies (the lowest-excited  $S_1$ , Q and B-band electronic states) for all monomers and D-A complexes calculated using B3LYP and OT-RSH functionals. All energies are in eV.

D-A Complex	$S_1$		Q-band		B-band	
	B3LYP	OT-RSH	B3LYP	OT-RSH	B3LYP	OT-RSH
PCBM	1.9	2.3	-	-	-	-
ZnPor	2.4	2.4	2.4	2.4	3.5	3.7
ZnChl	2.4	2.3	2.4	2.3	3.6	3.7
ZnBChl	2.0	1.9	2.1	1.9	3.8	3.9
ZnPor@PCBM	1.7	2.1	2.4	2.4	3.1	3.4
ZnChl@PCBM	1.3	1.9	2.3	2.3	3.1	3.5
ZnBChl@PCBM	0.8	1.3	2.0	2.0	4.0	3.9

**Table S5:** Calculated solvation energies considering both partial and full charge-separation (CS) for the lowest CT state (*i.e.*,  $CT_1$ ) in polar solvent DMF. Reorganization energies ( $\lambda_i$ ) obtained from DFT and CDFT methods considering a full CS are also listed for comparison. All energies are in eV.

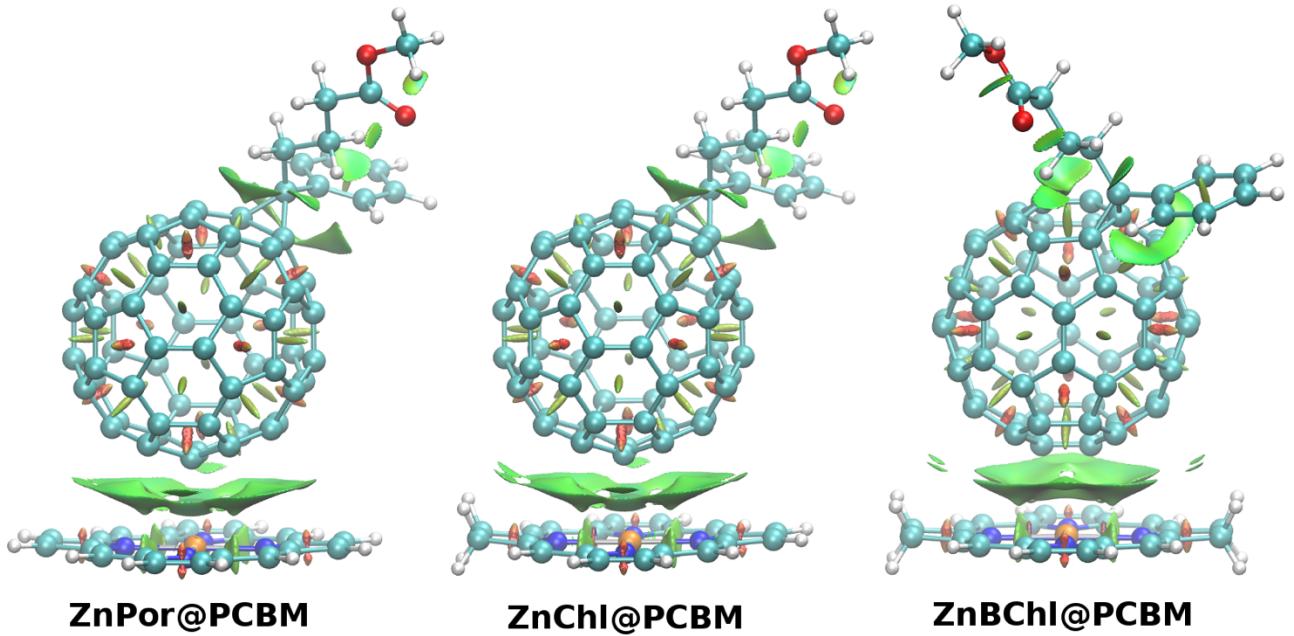
D-A Complex	Solvation Energy		$\lambda_i$	
	Partial CS	Full CS	DFT	CDFT
ZnPor@PCBM	0.05	0.45	0.143	0.234
ZnChl@PCBM	0.30	0.40	0.142	0.210
ZnBChl@PCBM	0.29	0.40	0.139	0.158

**Table S6:** Calculated reorganization energy for the D-A complex ( $\lambda_i$ ) using CDFT optimized CT-state geometry and for the solvent ( $\lambda_s$ ) using modified Marcus two-sphere model considering both partial and full charge-separation (CS) for the lowest CT electronic-state (*i.e.*,  $CT_1$ ) in polar solvent DMF. All energies are in eV.

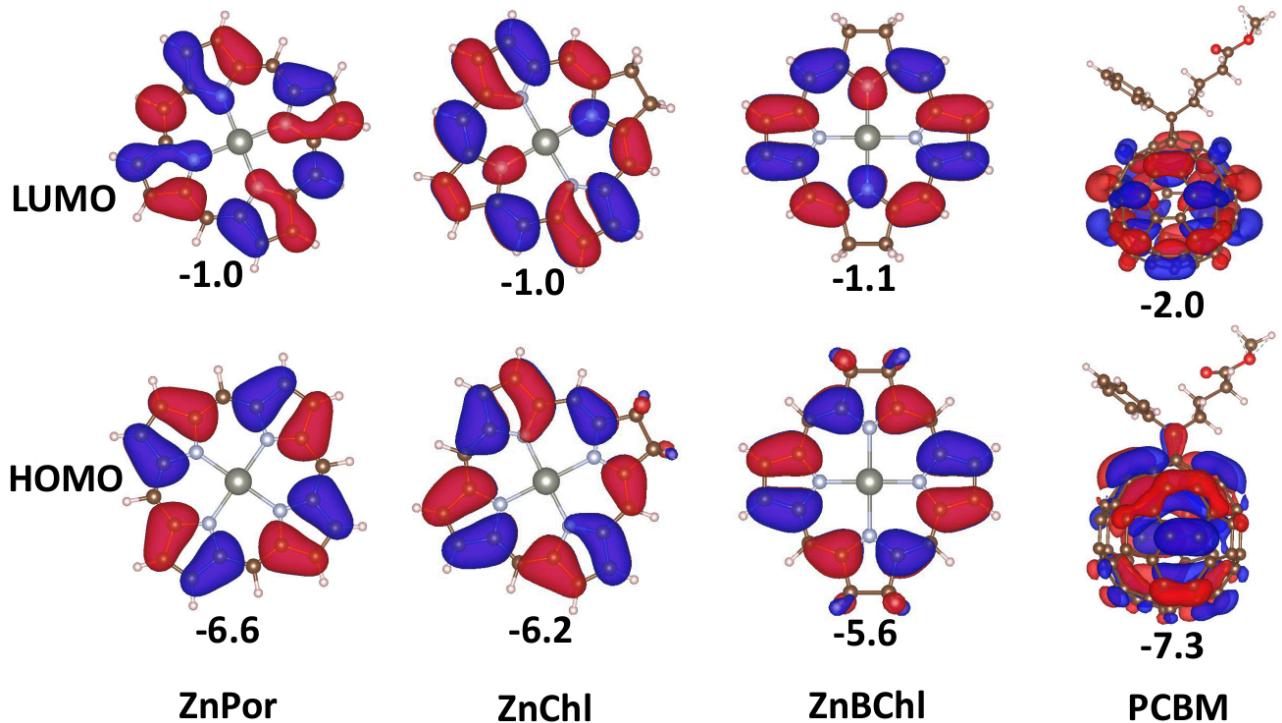
D-A Complex	$\lambda_i$		$\lambda_s$	
	Partial CS	Full CS	Partial CS	Full CS
ZnPor@PCBM	0.064	0.234	0.132	0.527
ZnChl@PCBM	0.176	0.210	0.428	0.528
ZnBChl@PCBM	0.131	0.158	0.432	0.534

**Table S7:** Calculated electronic couplings ( $V_{el}$ ), driving forces ( $\Delta E$ ), activation energy ( $E_a$ ) for CT in DMF, and also total reorganization energy ( $\lambda_r = \lambda_i + \lambda_s$ ) considering CDFT-optimized CT geometry for estimating  $\lambda_i$ , and the Marcus forward ( $k_f$ ) and backward ( $k_b$ ) CT rates (in  $s^{-1}$ ) calculated at 298 K considering CT-state associated with partial (values without bracket) and full CS (values within bracket). All energies are in eV.

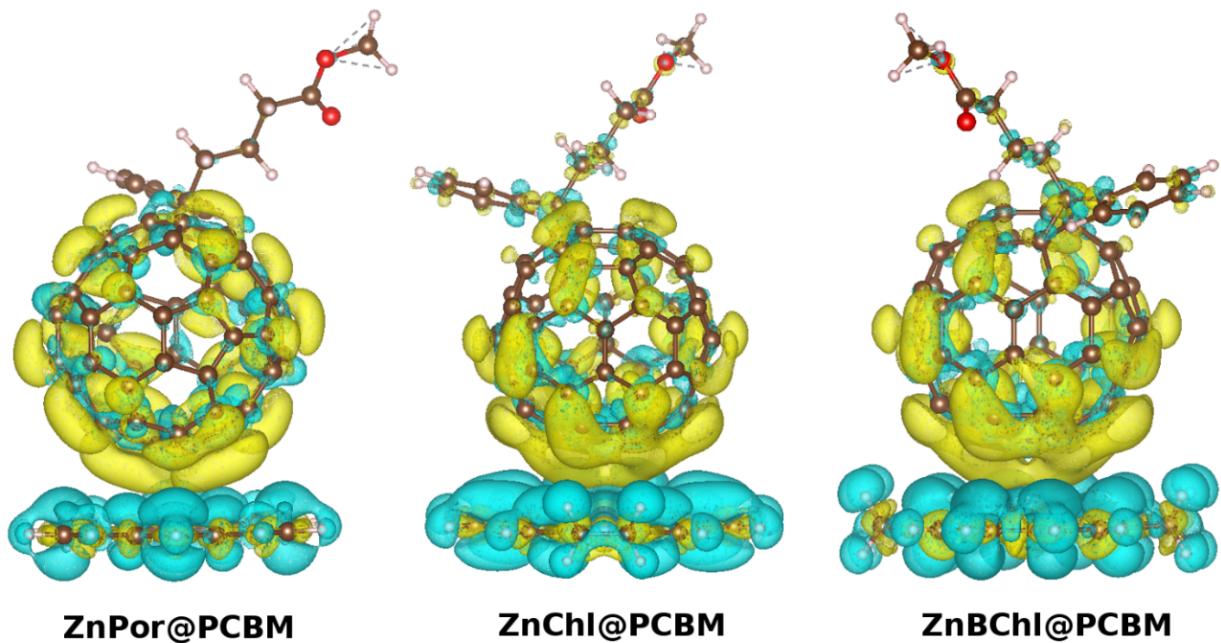
D-A Complex	$V_{el}$	$\Delta E$	$\lambda_r$	$E_a$	CT Rate		
					$k_f$	$k_b$	$\frac{k_f}{k_b}$
ZnPor@PCBM	0.012	0.414 (0.984)	0.196 (0.761)	0.061 (0.016)	$5.1 \times 10^{11}$ $(1.5 \times 10^{12})$	$5.1 \times 10^4$ $(3.3 \times 10^{-5})$	$1.0 \times 10^7$ $(4.5 \times 10^{16})$
ZnChl@PCBM	0.035	0.876 (1.010)	0.604 (0.738)	0.031 (0.025)	$8.0 \times 10^{12}$ $(9.0 \times 10^{12})$	$1.2 \times 10^{-2}$ $(7.5 \times 10^{-5})$	$6.7 \times 10^{14}$ $(1.2 \times 10^{17})$
ZnBChl@PCBM	0.026	1.121 (1.258)	0.563 (0.692)	0.138 (0.116)	$6.9 \times 10^{10}$ $(1.5 \times 10^{11})$	$7.6 \times 10^{-9}$ $(8.0 \times 10^{-11})$	$9.1 \times 10^{18}$ $(1.9 \times 10^{21})$



**Figure S1:** Non-covalent interactions (NCI) plots for all three D-A complexes. Blue, green and red coloured iso-surfaces indicate the strong, weak and repulsive interactions, respectively. An iso-value of  $0.004 \text{ e}/\text{\AA}^3$  is used. D-A interfacial green coloured iso-surfaces clearly suggest the presence of weak non-covalent dispersion interactions.



**Figure S2:** FMOs iso-surfaces for all monomers (isolated donors and acceptor) calculated using OT-RSH/6-31G (d). HOMO and LUMO energies are also listed in eV.



**Figure S3:** Localization of quasi-electron (yellow) and quasi-hole (cyan) densities in the lowest CT excited-state (*i.e.*,  $CT_1$ ) for the three D-A complexes calculated using OT-RSH/6-31G (d). An iso-value of  $0.0005 \text{ e}/\text{\AA}^3$  is used to plot these density iso-surfaces.