Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Photoinduced charge shift and charge recombination through an alkynyl spacer for an expanded acridinium-based dyad

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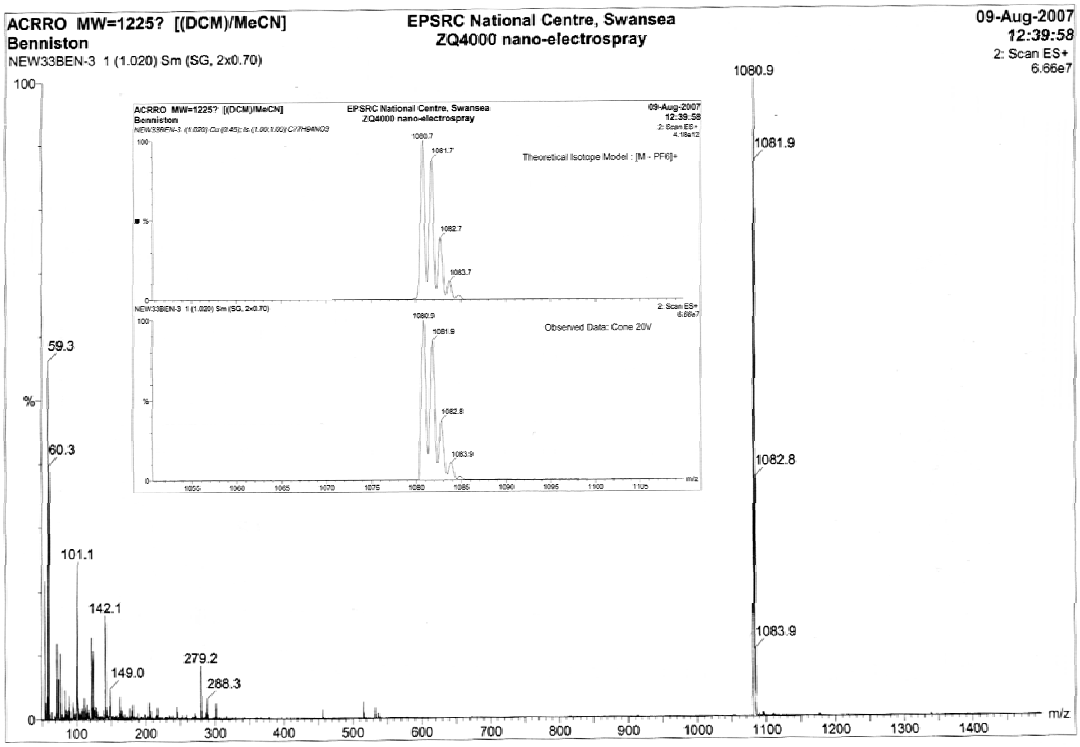
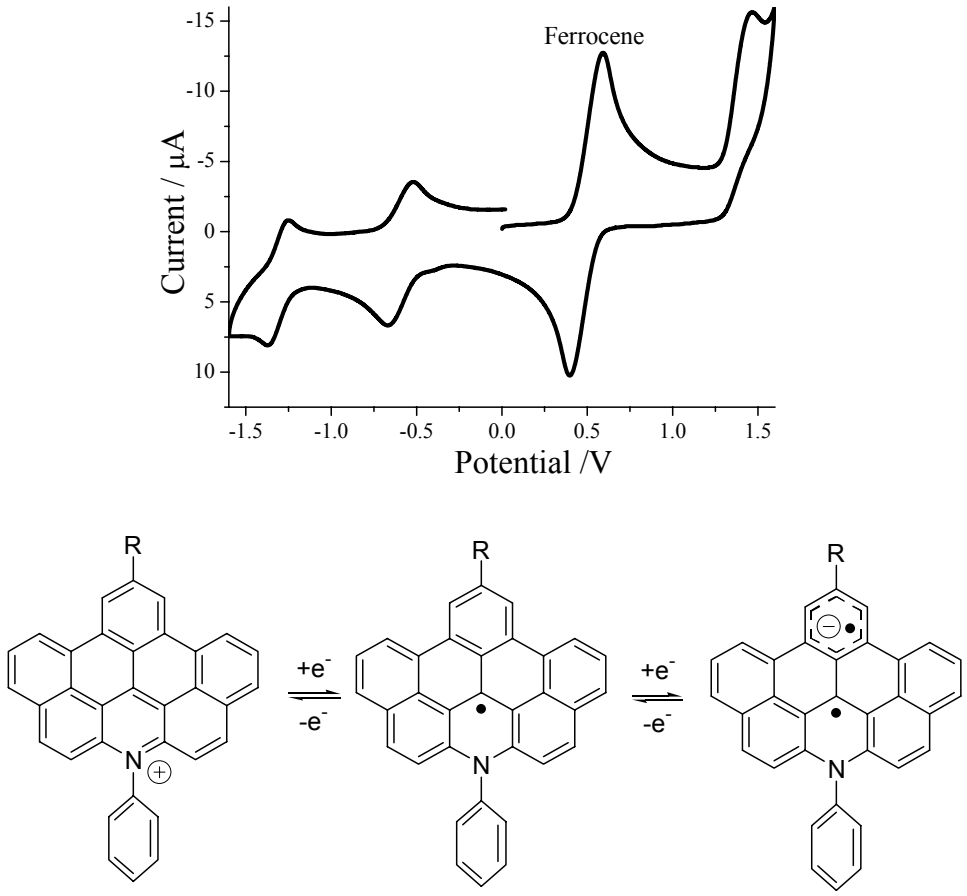
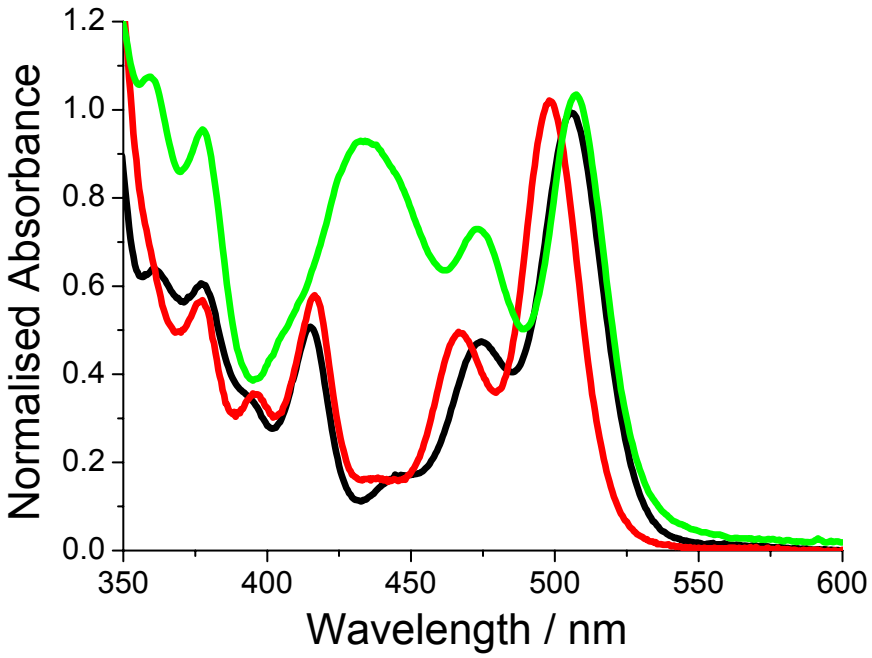


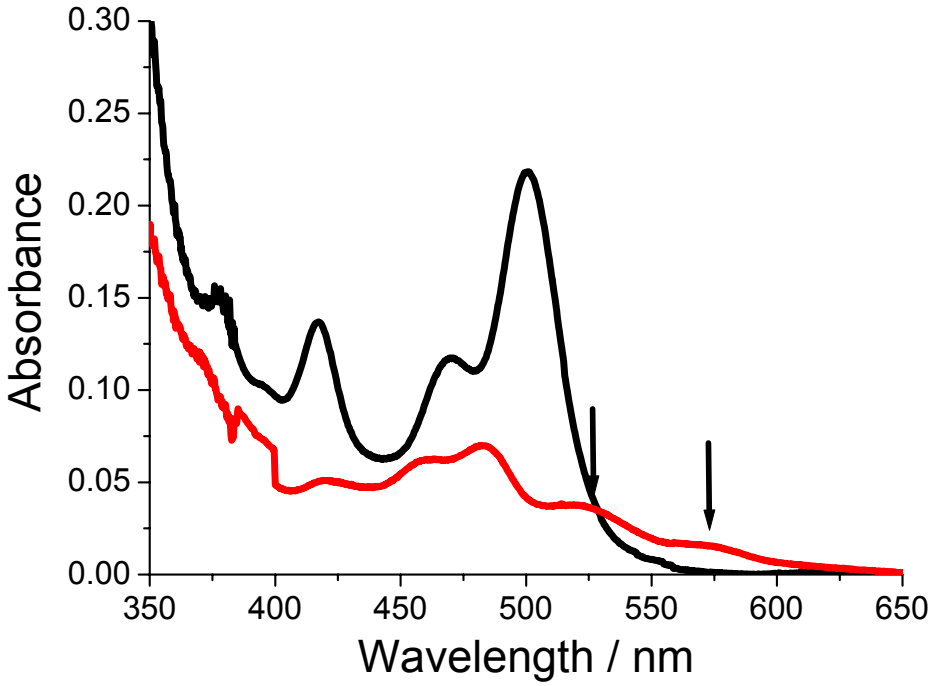
S1. Electrospray mass spectrum for **ACR**$^{+}$ and insert showing comparison of theoretical and found isotope pattern for the molecular ion.



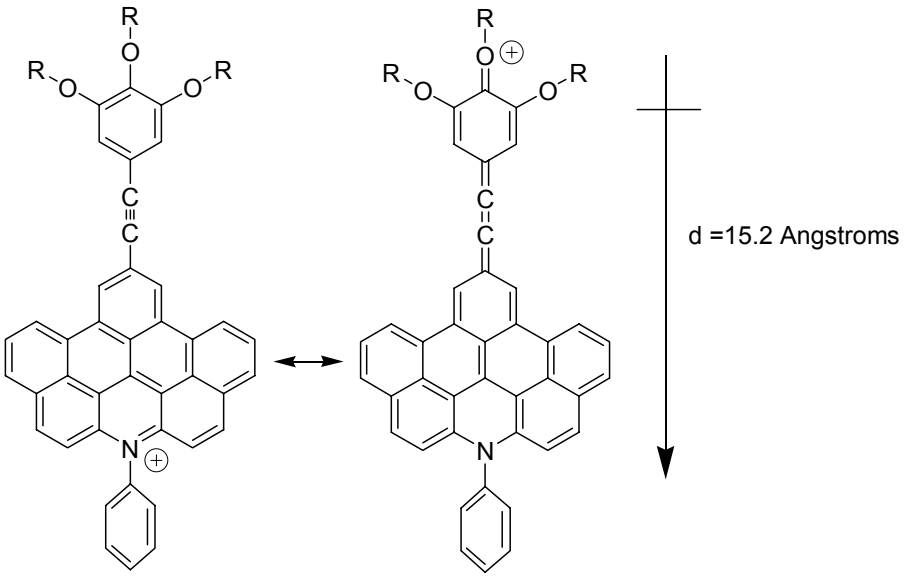
S2. Recorded cyclic voltammogram in dry CH_2Cl_2 (top) and representation of the molecular species generated by sequential addition of an electron (bottom) to **ACR**$^+$.



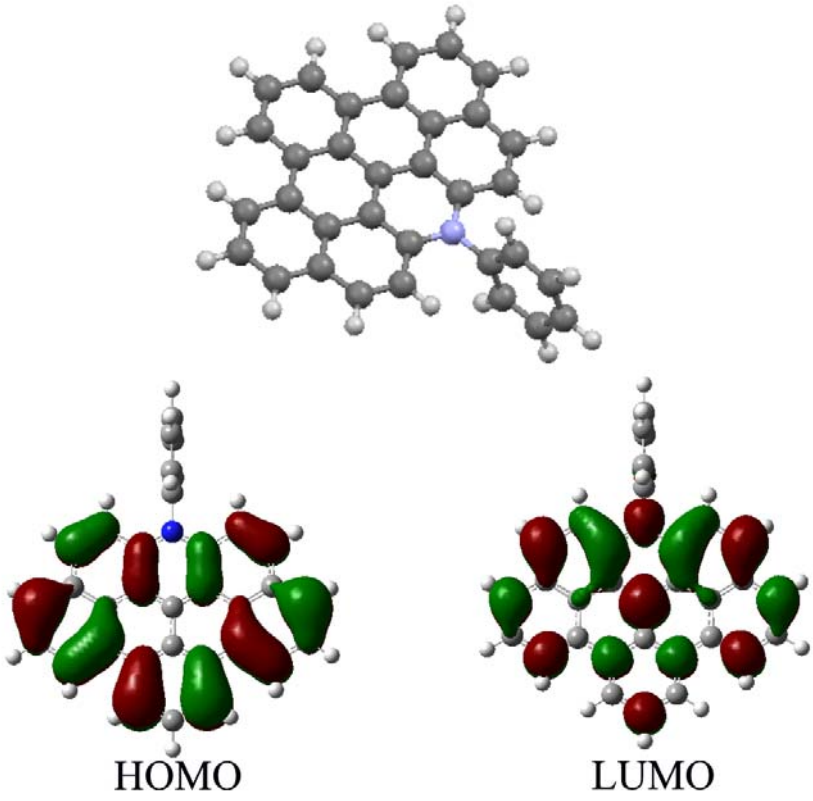
S3. Normalised absorption spectra for **1a** (red), **1b** (black) and **ACR**$^+$ (green) in dry CH_3CN.



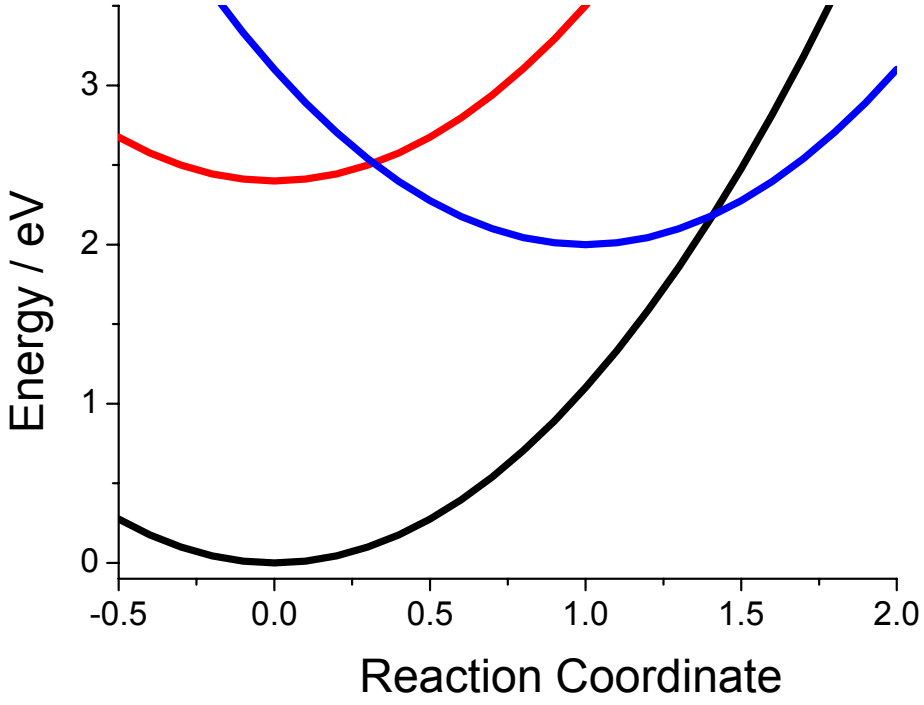
S4. Spectrolectrochemistry for **1a** in dry CH_3CN (0.2 M TBATFB) before (black) and after reduction (red). Arrows mark the broad long-wavelength absorption bands characteristic of the mono-reduced compound.



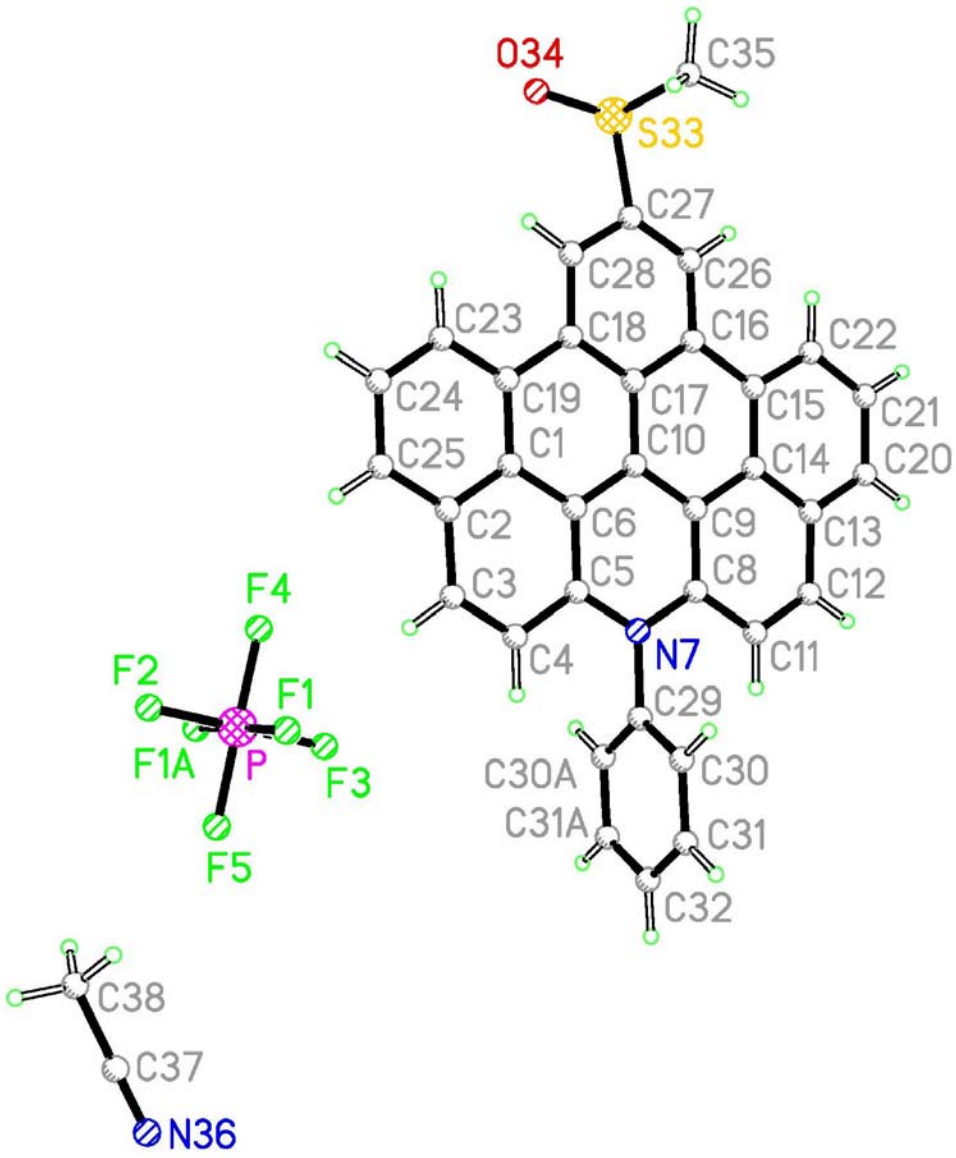
S5. Basic drawing of the charge shift state and the cumulene linking unit.



S6. Energy-minimised structure for **1b** (top) and the location of the HOMO and LUMO on the acridinium-based unit.



S7. Calculated potential energy surfaces for the ground state (black), first excited singlet state (red), and CSS (blue).



S8. X-ray crystallographic structure for the acetonitrile-solvated hexafluorophosphate salt of an expanded acridinium-based cation for which R = SOMe. Atoms with a suffix A are generated by crystallographic mirror symmetry. The SOMe substituent is disordered across this mirror plane, in which the whole condensed polyaromatic ring system lies. The anion and solvent molecule also lie on the mirror plane.

The cations are arranged in the crystal structure with graphitic stacking, the spacing between the precisely parallel planes being 3.40 Å (half the *b*-axis length).

Table S1. Crystal data and structure refinement for acb24.

Identification code	acb24	
Chemical formula (moiety)	$C_{34}H_{20}NOS^{+}\cdot PF_6^{-}\cdot C_2H_3N$	
Chemical formula (total)	$C_{36}H_{23}F_6N_2OPS$	
Formula weight	676.59	
Temperature	120(2) K	
Radiation, wavelength	synchrotron, 0.6709 Å	
Crystal system, space group	monoclinic, $P2_1/m$	
Unit cell parameters	a = 13.773(4) Å	α = 90°
	b = 6.7999(18) Å	β = 96.715(3)°
	c = 15.291(4) Å	γ = 90°
Cell volume	1422.3(7) Å^3	
Z	2	
Calculated density	1.580 g/cm^3	
Absorption coefficient μ	0.217 mm^{-1}	
F(000)	692	
Crystal colour and size	orange, 0.25 × 0.03 × 0.02 mm^3	
Reflections for cell refinement	2863 (θ range 2.5 to 28.6°)	
Data collection method	Bruker APEX2 CCD diffractometer	
	thin-slice ω scans	
θ range for data collection	3.5 to 23.5°	
Index ranges	h −16 to 16, k −8 to 8, l −18 to 18	
Completeness to θ = 23.5°	98.6 %	
Reflections collected	10624	
Independent reflections	2705 (R_{int} = 0.0508)	
Reflections with $F^2>2\sigma$	2070	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.948 and 0.996	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.1474, 0.7861	
Data / restraints / parameters	2705 / 0 / 283	
Final R indices [$F^2>2\sigma$]	R1 = 0.0755, wR2 = 0.2157	
R indices (all data)	R1 = 0.0909, wR2 = 0.2342	
Goodness-of-fit on F^2	1.051	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.61 and −0.36 e Å^{-3}	

Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for acb24. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
C(1)	0.4626(3)	0.2500	0.5291(3)	0.0345(8)
C(2)	0.3872(3)	0.2500	0.5842(3)	0.0387(9)
C(3)	0.4130(3)	0.2500	0.6770(3)	0.0429(10)
C(4)	0.5073(3)	0.2500	0.7138(3)	0.0449(10)
C(5)	0.5840(3)	0.2500	0.6587(2)	0.0387(9)
C(6)	0.5621(3)	0.2500	0.5670(2)	0.0346(9)
N(7)	0.6798(2)	0.2500	0.6957(2)	0.0423(8)
C(8)	0.7559(3)	0.2500	0.6453(3)	0.0405(9)
C(9)	0.7362(3)	0.2500	0.5531(2)	0.0359(9)
C(10)	0.6383(3)	0.2500	0.5128(2)	0.0325(8)
C(11)	0.8542(3)	0.2500	0.6856(3)	0.0528(12)
C(12)	0.9280(3)	0.2500	0.6352(3)	0.0556(12)
C(13)	0.9116(3)	0.2500	0.5416(3)	0.0492(11)
C(14)	0.8147(3)	0.2500	0.4994(3)	0.0377(9)
C(15)	0.7960(3)	0.2500	0.4076(2)	0.0383(9)
C(16)	0.6952(3)	0.2500	0.3658(2)	0.0365(9)
C(17)	0.6175(3)	0.2500	0.4196(2)	0.0347(8)
C(18)	0.5186(3)	0.2500	0.3806(2)	0.0376(9)
C(19)	0.4393(3)	0.2500	0.4368(2)	0.0369(9)
C(20)	0.9882(3)	0.2500	0.4910(3)	0.0594(13)
C(21)	0.9698(3)	0.2500	0.4003(3)	0.0586(13)
C(22)	0.8758(3)	0.2500	0.3588(3)	0.0459(10)
C(23)	0.3417(3)	0.2500	0.4027(3)	0.0419(10)
C(24)	0.2674(3)	0.2500	0.4572(3)	0.0440(10)
C(25)	0.2891(3)	0.2500	0.5468(3)	0.0426(10)
C(26)	0.6724(3)	0.2500	0.2755(3)	0.0479(10)
C(27)	0.5769(3)	0.2500	0.2389(3)	0.0572(13)
C(28)	0.5009(3)	0.2500	0.2897(3)	0.0568(13)
C(29)	0.7021(3)	0.2500	0.7915(3)	0.0510(11)
C(30)	0.7136(3)	0.4233(7)	0.8354(2)	0.0781(12)
C(31)	0.7377(4)	0.4228(9)	0.9253(2)	0.1005(17)
C(32)	0.7496(4)	0.2500	0.9689(3)	0.093(2)
S(33)	0.54917(13)	0.1866(3)	0.12237(10)	0.0669(9)
O(34)	0.4447(4)	0.1512(12)	0.1068(3)	0.126(4)
C(35)	0.5694(7)	0.4378(14)	0.0892(5)	0.083(3)
N(36)	0.1347(4)	0.2500	1.2438(3)	0.0719(13)
C(37)	0.0834(4)	0.2500	1.1806(3)	0.0650(14)
C(38)	0.0173(5)	0.2500	1.0984(4)	0.088(2)
P	0.16112(9)	0.2500	0.83155(7)	0.0548(5)
F(1)	0.1651(3)	0.4785(5)	0.8338(2)	0.1368(14)
F(2)	0.0481(2)	0.2500	0.8182(2)	0.137(2)
F(3)	0.2760(3)	0.2500	0.8455(2)	0.1230(18)
F(4)	0.1672(2)	0.2500	0.72902(17)	0.1063(15)
F(5)	0.1565(2)	0.2500	0.93415(16)	0.0827(11)

Table S3. Bond lengths [Å] and angles [°] for acb24.

C(1)–C(2)	1.413(5)	C(1)–C(6)	1.423(5)
C(1)–C(19)	1.410(5)	C(2)–C(3)	1.421(6)
C(2)–C(25)	1.404(6)	C(3)–H(3)	0.950
C(3)–C(4)	1.355(6)	C(4)–H(4)	0.950
C(4)–C(5)	1.426(5)	C(5)–C(6)	1.399(5)
C(5)–N(7)	1.374(5)	C(6)–C(10)	1.412(5)
N(7)–C(8)	1.373(5)	N(7)–C(29)	1.461(5)
C(8)–C(9)	1.403(5)	C(8)–C(11)	1.420(6)
C(9)–C(10)	1.416(5)	C(9)–C(14)	1.432(5)
C(10)–C(17)	1.421(5)	C(11)–H(11)	0.950
C(11)–C(12)	1.347(6)	C(12)–H(12)	0.950
C(12)–C(13)	1.422(6)	C(13)–C(14)	1.413(6)
C(13)–C(20)	1.379(6)	C(14)–C(15)	1.397(5)
C(15)–C(16)	1.460(6)	C(15)–C(22)	1.398(5)
C(16)–C(17)	1.424(5)	C(16)–C(26)	1.380(5)
C(17)–C(18)	1.421(5)	C(18)–C(19)	1.467(5)
C(18)–C(28)	1.383(6)	C(19)–C(23)	1.384(5)
C(20)–H(20)	0.950	C(20)–C(21)	1.381(6)
C(21)–H(21)	0.950	C(21)–C(22)	1.374(6)
C(22)–H(22)	0.950	C(23)–H(23)	0.950
C(23)–C(24)	1.393(6)	C(24)–H(24)	0.950
C(24)–C(25)	1.368(6)	C(25)–H(25)	0.950
C(26)–H(26)	0.950	C(26)–C(27)	1.367(6)
C(27)–C(28)	1.375(6)	C(27)–S(33)	1.829(4)
C(28)–H(28)	0.950	C(29)–C(30)	1.356(5)
C(29)–C(30A)	1.356(5)	C(30)–H(30)	0.950
C(30)–C(31)	1.375(5)	C(31)–H(31)	0.950
C(31)–C(32)	1.352(6)	C(32)–C(31A)	1.352(6)
C(32)–H(32)	0.950	S(33)–O(34)	1.450(6)
S(33)–C(35)	1.813(10)	C(35)–H(35A)	0.980
C(35)–H(35B)	0.980	C(35)–H(35C)	0.980
N(36)–C(37)	1.129(7)	C(37)–C(38)	1.463(8)
C(38)–H(38A)	0.980	C(38)–H(38B)	0.980
C(38)–H(38C)	0.980	P–F(1)	1.555(3)
P–F(1A)	1.555(3)	P–F(2)	1.546(3)
P–F(3)	1.571(4)	P–F(4)	1.580(3)
P–F(5)	1.578(3)		

C(2)–C(1)–C(6)	119.7(4)	C(2)–C(1)–C(19)	120.0(4)
C(6)–C(1)–C(19)	120.3(3)	C(1)–C(2)–C(3)	118.7(4)
C(1)–C(2)–C(25)	119.8(4)	C(3)–C(2)–C(25)	121.5(4)
C(2)–C(3)–H(3)	119.0	C(2)–C(3)–C(4)	122.1(4)
H(3)–C(3)–C(4)	119.0	C(3)–C(4)–H(4)	120.2
C(3)–C(4)–C(5)	119.6(4)	H(4)–C(4)–C(5)	120.2
C(4)–C(5)–C(6)	120.3(4)	C(4)–C(5)–N(7)	119.8(4)
C(6)–C(5)–N(7)	119.8(3)	C(1)–C(6)–C(5)	119.5(3)
C(1)–C(6)–C(10)	120.5(3)	C(5)–C(6)–C(10)	120.0(4)
C(5)–N(7)–C(8)	121.9(3)	C(5)–N(7)–C(29)	119.5(3)
C(8)–N(7)–C(29)	118.6(3)	N(7)–C(8)–C(9)	119.6(4)
N(7)–C(8)–C(11)	120.5(4)	C(9)–C(8)–C(11)	119.9(4)
C(8)–C(9)–C(10)	120.0(3)	C(8)–C(9)–C(14)	120.3(4)

C(10)–C(9)–C(14)	119.6(4)	C(6)–C(10)–C(9)	118.7(3)
C(6)–C(10)–C(17)	120.8(3)	C(9)–C(10)–C(17)	120.5(3)
C(8)–C(11)–H(11)	120.1	C(8)–C(11)–C(12)	119.7(4)
H(11)–C(11)–C(12)	120.1	C(11)–C(12)–H(12)	118.8
C(11)–C(12)–C(13)	122.3(4)	H(12)–C(12)–C(13)	118.8
C(12)–C(13)–C(14)	119.3(4)	C(12)–C(13)–C(20)	121.5(4)
C(14)–C(13)–C(20)	119.2(4)	C(9)–C(14)–C(13)	118.3(4)
C(9)–C(14)–C(15)	120.9(4)	C(13)–C(14)–C(15)	120.8(4)
C(14)–C(15)–C(16)	119.6(3)	C(14)–C(15)–C(22)	118.2(4)
C(16)–C(15)–C(22)	122.2(4)	C(15)–C(16)–C(17)	119.2(3)
C(15)–C(16)–C(26)	122.1(3)	C(17)–C(16)–C(26)	118.7(4)
C(10)–C(17)–C(16)	120.2(4)	C(10)–C(17)–C(18)	119.4(3)
C(16)–C(17)–C(18)	120.4(3)	C(17)–C(18)–C(19)	119.9(3)
C(17)–C(18)–C(28)	117.9(4)	C(19)–C(18)–C(28)	122.2(4)
C(1)–C(19)–C(18)	119.2(3)	C(1)–C(19)–C(23)	118.4(3)
C(18)–C(19)–C(23)	122.4(4)	C(13)–C(20)–H(20)	120.0
C(13)–C(20)–C(21)	120.1(4)	H(20)–C(20)–C(21)	120.0
C(20)–C(21)–H(21)	119.5	C(20)–C(21)–C(22)	121.0(4)
H(21)–C(21)–C(22)	119.5	C(15)–C(22)–C(21)	120.7(4)
C(15)–C(22)–H(22)	119.6	C(21)–C(22)–H(22)	119.6
C(19)–C(23)–H(23)	119.2	C(19)–C(23)–C(24)	121.5(4)
H(23)–C(23)–C(24)	119.2	C(23)–C(24)–H(24)	119.7
C(23)–C(24)–C(25)	120.6(4)	H(24)–C(24)–C(25)	119.7
C(2)–C(25)–C(24)	119.7(4)	C(2)–C(25)–H(25)	120.1
C(24)–C(25)–H(25)	120.1	C(16)–C(26)–H(26)	119.8
C(16)–C(26)–C(27)	120.4(4)	H(26)–C(26)–C(27)	119.8
C(26)–C(27)–C(28)	121.8(4)	C(26)–C(27)–S(33)	118.7(3)
C(28)–C(27)–S(33)	117.7(3)	C(18)–C(28)–C(27)	120.8(4)
C(18)–C(28)–H(28)	119.6	C(27)–C(28)–H(28)	119.6
N(7)–C(29)–C(30)	119.7(2)	N(7)–C(29)–C(30A)	119.7(2)
C(30)–C(29)–C(30A)	120.7(5)	C(29)–C(30)–H(30)	120.2
C(29)–C(30)–C(31)	119.5(5)	H(30)–C(30)–C(31)	120.2
C(30)–C(31)–H(31)	120.1	C(30)–C(31)–C(32)	119.8(5)
H(31)–C(31)–C(32)	120.1	C(31)–C(32)–C(31A)	120.8(5)
C(31)–C(32)–H(32)	119.6	C(31A)–C(32)–H(32)	119.6
C(27)–S(33)–O(34)	106.8(3)	C(27)–S(33)–C(35)	91.6(3)
O(34)–S(33)–C(35)	107.0(5)	S(33)–C(35)–H(35A)	109.5
S(33)–C(35)–H(35B)	109.5	S(33)–C(35)–H(35C)	109.5
H(35A)–C(35)–H(35B)	109.5	H(35A)–C(35)–H(35C)	109.5
H(35B)–C(35)–H(35C)	109.5	N(36)–C(37)–C(38)	179.7(5)
C(37)–C(38)–H(38A)	109.5	C(37)–C(38)–H(38B)	109.5
C(37)–C(38)–H(38C)	109.5	H(38A)–C(38)–H(38B)	109.5
H(38A)–C(38)–H(38C)	109.5	H(38B)–C(38)–H(38C)	109.5
F(1)–P–F(1A)	175.5(3)	F(1)–P–F(2)	92.00(15)
F(1A)–P–F(2)	92.00(15)	F(1)–P–F(3)	88.00(15)
F(1A)–P–F(3)	87.99(15)	F(1)–P–F(4)	90.93(11)
F(1A)–P–F(4)	90.93(11)	F(1)–P–F(5)	89.05(12)
F(1A)–P–F(5)	89.05(12)	F(2)–P–F(3)	179.81(18)
F(2)–P–F(4)	92.17(17)	F(2)–P–F(5)	88.55(18)
F(3)–P–F(4)	88.02(18)	F(3)–P–F(5)	91.26(18)
F(4)–P–F(5)	179.28(18)		

Symmetry operation for equivalent atoms: A x, –y+1/2, z

Table S4. Anisotropic displacement parameters ($Å^2$) for acb24. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	0.035(2)	0.0305(19)	0.040(2)	0.000	0.0116(16)	0.000
C(2)	0.043(2)	0.036(2)	0.040(2)	0.000	0.0176(17)	0.000
C(3)	0.041(2)	0.048(2)	0.043(2)	0.000	0.0227(17)	0.000
C(4)	0.052(2)	0.058(3)	0.0279(19)	0.000	0.0197(17)	0.000
C(5)	0.040(2)	0.044(2)	0.034(2)	0.000	0.0111(16)	0.000
C(6)	0.042(2)	0.036(2)	0.0283(19)	0.000	0.0149(15)	0.000
N(7)	0.0439(19)	0.061(2)	0.0235(16)	0.000	0.0110(13)	0.000
C(8)	0.039(2)	0.053(2)	0.031(2)	0.000	0.0108(16)	0.000
C(9)	0.040(2)	0.042(2)	0.0282(19)	0.000	0.0131(15)	0.000
C(10)	0.0337(19)	0.0326(19)	0.0327(19)	0.000	0.0106(15)	0.000
C(11)	0.049(2)	0.084(3)	0.026(2)	0.000	0.0074(17)	0.000
C(12)	0.036(2)	0.094(4)	0.037(2)	0.000	0.0076(17)	0.000
C(13)	0.044(2)	0.068(3)	0.038(2)	0.000	0.0149(18)	0.000
C(14)	0.039(2)	0.043(2)	0.034(2)	0.000	0.0149(16)	0.000
C(15)	0.042(2)	0.042(2)	0.033(2)	0.000	0.0144(16)	0.000
C(16)	0.041(2)	0.039(2)	0.0313(19)	0.000	0.0129(16)	0.000
C(17)	0.043(2)	0.035(2)	0.0279(18)	0.000	0.0127(15)	0.000
C(18)	0.037(2)	0.041(2)	0.036(2)	0.000	0.0082(16)	0.000
C(19)	0.042(2)	0.035(2)	0.035(2)	0.000	0.0103(16)	0.000
C(20)	0.034(2)	0.099(4)	0.048(3)	0.000	0.0166(19)	0.000
C(21)	0.041(2)	0.099(4)	0.039(2)	0.000	0.0207(18)	0.000
C(22)	0.044(2)	0.061(3)	0.036(2)	0.000	0.0184(17)	0.000
C(23)	0.040(2)	0.045(2)	0.042(2)	0.000	0.0085(17)	0.000
C(24)	0.037(2)	0.048(2)	0.049(2)	0.000	0.0095(17)	0.000
C(25)	0.038(2)	0.040(2)	0.053(2)	0.000	0.0208(18)	0.000
C(26)	0.048(2)	0.067(3)	0.031(2)	0.000	0.0159(17)	0.000
C(27)	0.046(2)	0.098(4)	0.030(2)	0.000	0.0098(18)	0.000
C(28)	0.042(2)	0.096(4)	0.033(2)	0.000	0.0058(18)	0.000
C(29)	0.043(2)	0.084(3)	0.028(2)	0.000	0.0109(17)	0.000
C(30)	0.092(3)	0.109(3)	0.0347(17)	–0.0159(19)	0.0155(17)	–0.033(2)
C(31)	0.115(4)	0.154(5)	0.035(2)	–0.022(2)	0.016(2)	–0.050(3)
C(32)	0.063(3)	0.190(8)	0.029(3)	0.000	0.012(2)	0.000
S(33)	0.0615(10)	0.115(3)	0.0247(7)	–0.0071(8)	0.0070(6)	–0.0108(9)
O(34)	0.083(4)	0.260(13)	0.036(2)	–0.020(4)	0.011(2)	–0.042(5)
C(35)	0.114(7)	0.105(7)	0.034(3)	0.029(4)	0.029(4)	0.021(5)
N(36)	0.069(3)	0.100(4)	0.051(3)	0.000	0.024(2)	0.000
C(37)	0.059(3)	0.093(4)	0.049(3)	0.000	0.030(2)	0.000
C(38)	0.078(4)	0.141(6)	0.048(3)	0.000	0.021(3)	0.000
P	0.0539(8)	0.0898(10)	0.0226(6)	0.000	0.0131(5)	0.000
F(1)	0.212(4)	0.095(2)	0.120(3)	0.0253(17)	0.092(3)	0.012(2)
F(2)	0.0494(19)	0.322(7)	0.0421(18)	0.000	0.0083(14)	0.000
F(3)	0.063(2)	0.253(6)	0.054(2)	0.000	0.0112(16)	0.000
F(4)	0.070(2)	0.229(5)	0.0229(14)	0.000	0.0194(13)	0.000
F(5)	0.095(2)	0.131(3)	0.0252(14)	0.000	0.0183(13)	0.000

Table S5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for acb24.

	x	y	z	U
H(3)	0.3625	0.2500	0.7143	0.051
H(4)	0.5224	0.2500	0.7761	0.054
H(11)	0.8677	0.2500	0.7480	0.063
H(12)	0.9934	0.2500	0.6631	0.067
H(20)	1.0537	0.2500	0.5186	0.071
H(21)	1.0230	0.2500	0.3660	0.070
H(22)	0.8648	0.2500	0.2963	0.055
H(23)	0.3249	0.2500	0.3406	0.050
H(24)	0.2010	0.2500	0.4319	0.053
H(25)	0.2381	0.2500	0.5836	0.051
H(26)	0.7233	0.2500	0.2386	0.057
H(28)	0.4355	0.2500	0.2621	0.068
H(30)	0.7050	0.5442	0.8043	0.094
H(31)	0.7459	0.5435	0.9566	0.121
H(32)	0.7666	0.2500	1.0309	0.112
H(35A)	0.5590	0.4473	0.0249	0.124
H(35B)	0.6365	0.4769	0.1103	0.124
H(35C)	0.5235	0.5252	0.1146	0.124
H(38A)	–0.0506	0.2500	1.1118	0.106
H(38B)	0.0291	0.1323	1.0641	0.106
H(38C)	0.0291	0.3677	1.0641	0.106

Table S6. Torsion angles [°] for acb24.

C(6)–C(1)–C(2)–C(3)	0.0	C(6)–C(1)–C(2)–C(25)	180.0
C(19)–C(1)–C(2)–C(3)	180.0	C(19)–C(1)–C(2)–C(25)	0.0
C(1)–C(2)–C(3)–C(4)	0.0	C(25)–C(2)–C(3)–C(4)	180.0
C(2)–C(3)–C(4)–C(5)	0.0	C(3)–C(4)–C(5)–C(6)	0.0
C(3)–C(4)–C(5)–N(7)	180.0	C(4)–C(5)–C(6)–C(1)	0.0
C(4)–C(5)–C(6)–C(10)	180.0	N(7)–C(5)–C(6)–C(1)	180.0
N(7)–C(5)–C(6)–C(10)	0.0	C(2)–C(1)–C(6)–C(5)	0.0
C(2)–C(1)–C(6)–C(10)	180.0	C(19)–C(1)–C(6)–C(5)	180.0
C(19)–C(1)–C(6)–C(10)	0.0	C(4)–C(5)–N(7)–C(8)	180.0
C(4)–C(5)–N(7)–C(29)	0.0	C(6)–C(5)–N(7)–C(8)	0.0
C(6)–C(5)–N(7)–C(29)	180.0	C(5)–N(7)–C(8)–C(9)	0.0
C(5)–N(7)–C(8)–C(11)	180.0	C(29)–N(7)–C(8)–C(9)	180.0
C(29)–N(7)–C(8)–C(11)	0.0	N(7)–C(8)–C(9)–C(10)	0.0
N(7)–C(8)–C(9)–C(14)	180.0	C(11)–C(8)–C(9)–C(10)	180.0
C(11)–C(8)–C(9)–C(14)	0.0	C(1)–C(6)–C(10)–C(9)	180.0
C(1)–C(6)–C(10)–C(17)	0.0	C(5)–C(6)–C(10)–C(9)	0.0
C(5)–C(6)–C(10)–C(17)	180.0	C(8)–C(9)–C(10)–C(6)	0.0
C(8)–C(9)–C(10)–C(17)	180.0	C(14)–C(9)–C(10)–C(6)	180.0
C(14)–C(9)–C(10)–C(17)	0.0	N(7)–C(8)–C(11)–C(12)	180.0
C(9)–C(8)–C(11)–C(12)	0.0	C(8)–C(11)–C(12)–C(13)	0.0
C(11)–C(12)–C(13)–C(14)	0.0	C(11)–C(12)–C(13)–C(20)	180.0
C(12)–C(13)–C(14)–C(9)	0.0	C(12)–C(13)–C(14)–C(15)	180.0
C(20)–C(13)–C(14)–C(9)	180.0	C(20)–C(13)–C(14)–C(15)	0.0
C(8)–C(9)–C(14)–C(13)	0.0	C(8)–C(9)–C(14)–C(15)	180.0
C(10)–C(9)–C(14)–C(13)	180.0	C(10)–C(9)–C(14)–C(15)	0.0
C(9)–C(14)–C(15)–C(16)	0.0	C(9)–C(14)–C(15)–C(22)	180.0
C(13)–C(14)–C(15)–C(16)	180.0	C(13)–C(14)–C(15)–C(22)	0.0
C(14)–C(15)–C(16)–C(17)	0.0	C(14)–C(15)–C(16)–C(26)	180.0
C(22)–C(15)–C(16)–C(17)	180.0	C(22)–C(15)–C(16)–C(26)	0.0
C(6)–C(10)–C(17)–C(16)	180.0	C(6)–C(10)–C(17)–C(18)	0.0
C(9)–C(10)–C(17)–C(16)	0.0	C(9)–C(10)–C(17)–C(18)	180.0
C(15)–C(16)–C(17)–C(10)	0.0	C(15)–C(16)–C(17)–C(18)	180.0
C(26)–C(16)–C(17)–C(10)	180.0	C(26)–C(16)–C(17)–C(18)	0.0
C(10)–C(17)–C(18)–C(19)	0.0	C(10)–C(17)–C(18)–C(28)	180.0
C(16)–C(17)–C(18)–C(19)	180.0	C(16)–C(17)–C(18)–C(28)	0.0
C(2)–C(1)–C(19)–C(18)	180.0	C(2)–C(1)–C(19)–C(23)	0.0
C(6)–C(1)–C(19)–C(18)	0.0	C(6)–C(1)–C(19)–C(23)	180.0
C(17)–C(18)–C(19)–C(1)	0.0	C(17)–C(18)–C(19)–C(23)	180.0
C(28)–C(18)–C(19)–C(1)	180.0	C(28)–C(18)–C(19)–C(23)	0.0
C(12)–C(13)–C(20)–C(21)	180.0	C(14)–C(13)–C(20)–C(21)	0.0
C(13)–C(20)–C(21)–C(22)	0.0	C(20)–C(21)–C(22)–C(15)	0.0
C(14)–C(15)–C(22)–C(21)	0.0	C(16)–C(15)–C(22)–C(21)	180.0
C(1)–C(19)–C(23)–C(24)	0.0	C(18)–C(19)–C(23)–C(24)	180.0
C(19)–C(23)–C(24)–C(25)	0.0	C(23)–C(24)–C(25)–C(2)	0.0
C(1)–C(2)–C(25)–C(24)	0.0	C(3)–C(2)–C(25)–C(24)	180.0
C(15)–C(16)–C(26)–C(27)	180.0	C(17)–C(16)–C(26)–C(27)	0.0
C(16)–C(26)–C(27)–C(28)	0.0	C(16)–C(26)–C(27)–S(33)	–164.40(10)
C(26)–C(27)–C(28)–C(18)	0.0	S(33)–C(27)–C(28)–C(18)	164.56(10)
C(17)–C(18)–C(28)–C(27)	0.0	C(19)–C(18)–C(28)–C(27)	180.0
C(5)–N(7)–C(29)–C(30)	–90.8(4)	C(5)–N(7)–C(29)–C(30A)	90.8(4)
C(8)–N(7)–C(29)–C(30)	89.2(4)	C(8)–N(7)–C(29)–C(30A)	–89.2(4)

N(7)–C(29)–C(30)–C(31)	–177.9(4)	C(30A)–C(29)–C(30)–C(31)	0.4(8)
C(29)–C(30)–C(31)–C(32)	–0.1(7)	C(30)–C(31)–C(32)–C(31A)	–0.3(10)
C(26)–C(27)–S(33)–O(34)	166.3(4)	C(26)–C(27)–S(33)–C(35)	–85.4(3)
C(28)–C(27)–S(33)–O(34)	1.3(4)	C(28)–C(27)–S(33)–C(35)	109.6(3)

Symmetry operations for equivalent atoms: A x, –y+1/2, z

S9. According to the Rehm-Weller equation the free energy change for electron transfer is given by:

$$\Delta G^{0}_{et} = F(E_D - E_A) - E_{oo} + \Delta G_s + W \quad \text{(Eq. 1)}$$

$$\Delta G_s = \frac{nq^2}{8\pi\varepsilon_0}\left(\frac{2Z_D + n}{r_D}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_D}\right) - \frac{2Z_A - n}{r_A}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_A}\right)\right) \text{(Eq. 2)}$$

$$W = \frac{n(Z_A - Z_D - n)q^2}{4\pi\varepsilon_0\varepsilon R_{DA}} \text{(Eq.3)}$$

Here Z_A and Z_D refer to the charge on the acceptor and donor prior to electron transfer. The full definition of the terms can be found in reference 1. ΔG_s represents the Born solvation term and W is the Coulombic correction.

Evidently when $Z_A = 1$, $Z_D = 0$ and $n = 1$, as in the case for **ACR**$^+$, then if follows that:

$$W = \frac{1(1-0-1)q^2}{4\pi\varepsilon_0\varepsilon R_{DA}} = 0$$

Taking the same case as above for which $\varepsilon_D = \varepsilon_A = \varepsilon_{elec}$, and this final term represents the solvent in which the electrochemistry experiment was performed, affords the following equation:

$$\Delta G_s = \frac{q^2}{8\pi\varepsilon_0}\left(\frac{1}{r_D}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{elec}}\right) - \frac{1}{r_A}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{elec}}\right)\right) \text{(Eq.4)}$$

Rearranging gives:

$$\Delta G_s = \frac{q^2}{4\pi\varepsilon_0}\left(\left(\frac{1}{2r_D} - \frac{1}{2r_A}\right)\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{elec}}\right)\right) \text{(Eq.5)}$$

This equation is slightly different that where charge transfer takes place to generate a fully separated radical cation and radical anion pair. Here, the reciprocals for the diameter terms are added.

Clearly if $r_D = r_A$ then $\Delta G_s = 0$.

If $r_A \sim 2r_D$, which is the approximate case for **ACR**$^+$, then the equation becomes:

$$\Delta G_s = \frac{q^2}{4\pi\varepsilon_0}\left(\left(\frac{1}{2r_D} - \frac{1}{4r_D}\right)\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{elec}}\right)\right) \text{(Eq.6)}$$

which simplifies to:

$$\Delta G_s = \frac{q^2}{8\pi\varepsilon_0}\left(\left(\frac{1}{2r_D}\right)\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{elec}}\right)\right) \text{(Eq.7)}$$

assuming that $\varepsilon >> \varepsilon_{elec}$ then is follows that:

$$\Delta G_s = \frac{q^2}{8\pi\varepsilon_0\varepsilon}\left(\left(\frac{1}{2r_D}\right)\right) \text{(Eq.8)}$$

Clearly this assumption assumes that the dielectric constant, ε_{elec}, is identical to the neat solvent in which the electrochemistry experiment was performed. This is not necessarily the case since the solvent contains a considerable concentration of background electrolyte. For example, the dielectric constant for CH_2Cl_2 containing 0.2 M TBATFB was calculated to be 18.0 rather than 8.93 for the neat solvent.[1]

Taking this new value for CH_2Cl_2 then it follows for **ACR**$^+$ that the term:

$$\Delta G_s = \left(\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{elec}}\right)\right) = 0.04 \text{ using } \varepsilon = 10.36 \text{ (the solvent for the time resolved studies)}$$

Given that $r_D = 2.45$ Å then it follows that:

$$\Delta G_s = \frac{(1.602\text{x}10^{-19})^2}{8 \text{ x } 3.142 \text{ x } 8.854 \text{ x}10^{-12}}\left(\left(\frac{1}{4.9\text{x}10^{-10}}\right)(0.04)\right)$$

$$= 0.06\text{eV (60 mV)}$$

Alternatively, it seem reasonable to assume that $\Delta G_s \sim 0$ since $\varepsilon \sim \varepsilon_{elec}$.

Reference

1: D. Bao, B. Millare, W. Xia, B. G. Steyer, A. A. Gerasimenko, A. Ferreira, A. Contreras and V. I. Vullev, *J. Phys. Chem. A* 2009, **113**, 1259.