**Electronic Supplementary Information for PCCP article**

# Counter-Ion Modulation of the Long-Distance π-Bonding of the Open-Shell *p*-Benzoquinone Anions

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Molecular structures of [{K(dibenzo-18-crown-6)**DDQ}$_2$], **[{**K(18-crown-6)**DDQ}$_2$**], **[{**Na(15-crown-5)**CA}$_2$**], [(K(15-crown-5)$_2$]**CA, [**K(18-crown-6) (THF)$_2$]**CA** and **[{**K(18-crown-6)**CA}$_2$**]$O_n$; concentration- and temperature-dependencies of the absorption spectra of Na(15-crown-5)**DDQ** and Na(15-crown-5)**CA** salts in dichloromethane,solid-state spectra of **DDQ** dimers, atomic charges residing on the anionic **DDQ** moieties, bondlengths of neutral and anionic (π-bonded and monomeric) **DDQ** and **CA** moieties, Gaussian 98 comoputations of energies of multi-ion assemblies of π-bonded **DDQ** anions, details of the coulombic force computations, crystallographic parameters and the details of the structure refinements.

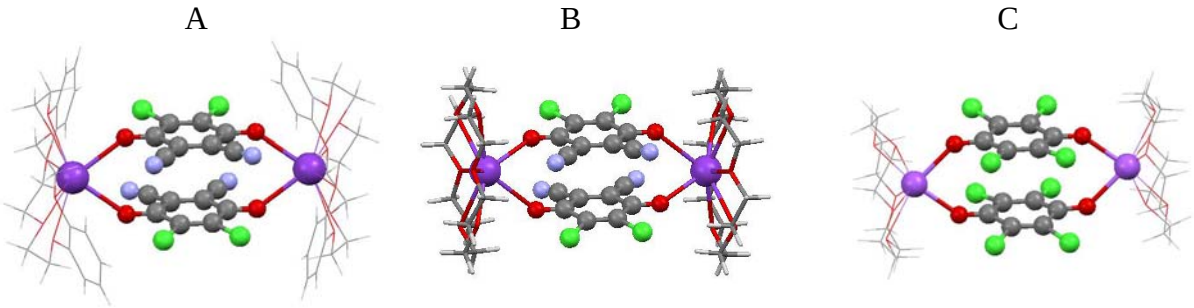



Figure S1. Molecular structures of the [{K(dibenzo-18-crown-6)**DDQ}**$_2$] (A) **,** **[{**K(18-crown-6)**DDQ}**$_2$] (B) , and **[{**Na(15-crown-5)**CA}**$_2$] (C) complexes.

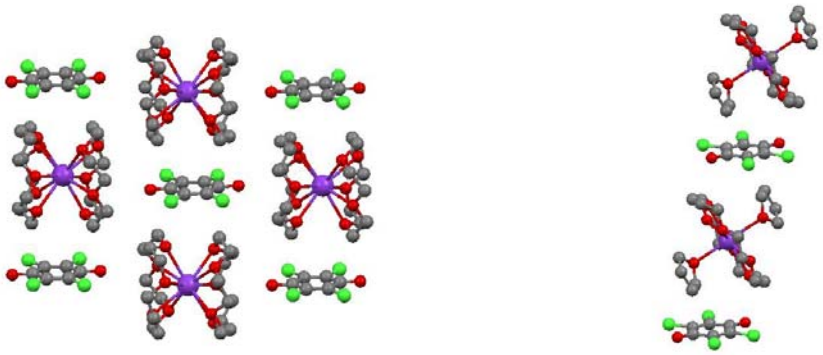


Figure S2. Crystal lattice of the [K(15-crown-5)$_2$]**CA** (left) and [K(18-crown-6)(THF)$_2$]**CA** (right) salts showing separated monomeric chloranil anion-radical.

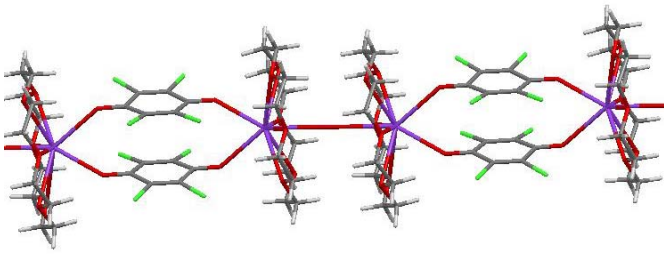


Figure S3. Molecular structure of **[{**K(18-crown-6)**CA}**$_2$]$O_n$ salt (n<1).

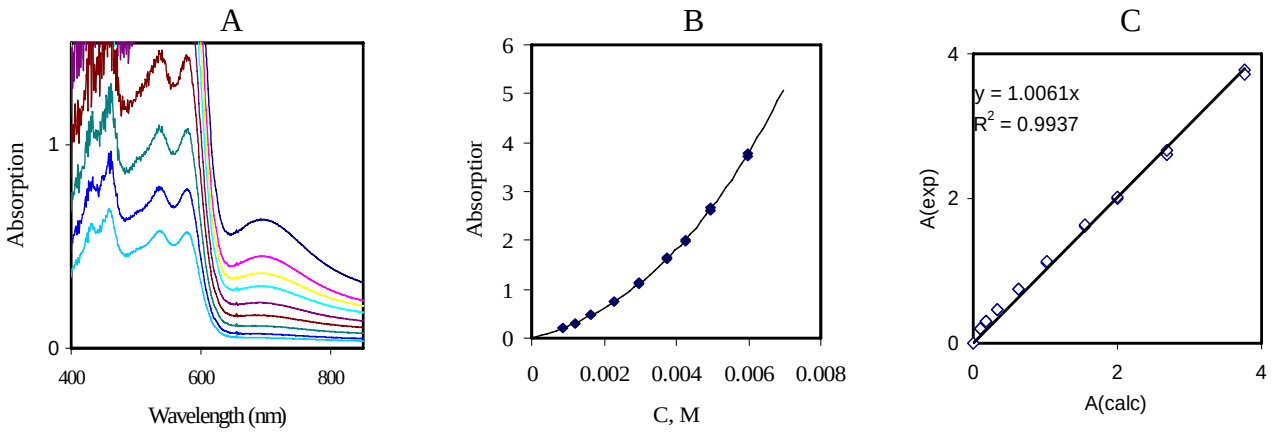



Figure S4. (A) Concentration dependence of the absorption of solution of Na(15-crown-5)**DDQ** salt in $CH_2Cl_2$ at 22°C. B) Quadrtatic approximation of the absorption of 695 nm band of these solutions. C) Relationship between experimental absorption of 695 nm and the values of absorption calculated for the dimerization process in eq 3 with $\varepsilon_D = 2.3\times10^4$ and $K_D = 5$.

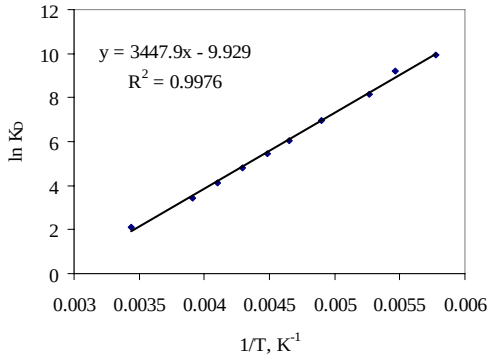



Figure S5. Temperature dependence of equilibrium constant of dimer formation in eq 1 in the solutions of contact ion-pairs salt Na(15-crown-5)**DDQ**.

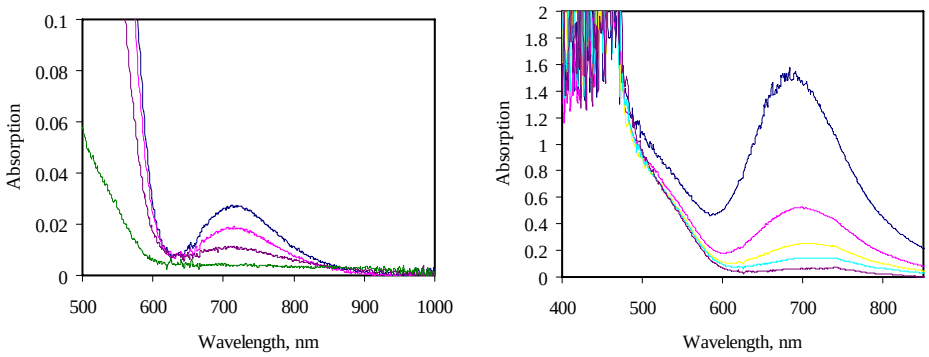



Figure S6. UV-Vis absorption of the solution of Na(15-crown-5)**CA** salt in $CH_2Cl_2$ showing the dimers band at $\lambda_{max}$ ~700 nm at high concentration and low temperatures. A) Salt concentrations (mM): 1.0, 4.3, 7.2, 8.6 at 22°C. B) Temperatures (°C): 20, -5, -30, -60, -90 (2 mM solution).

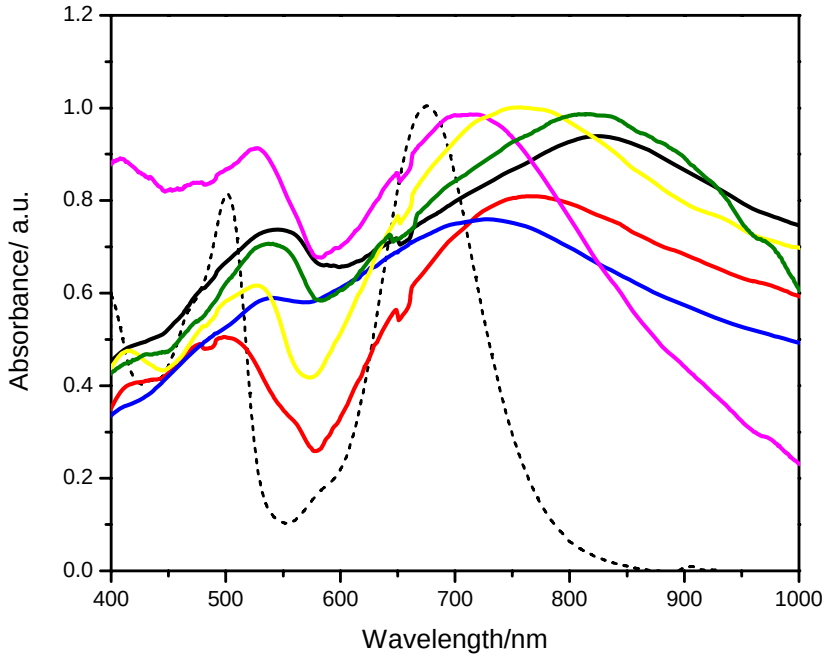



Figure S7. Solid state spectra of **DDQ** dimers (measured in nujol oil): [{K(18-crown-6)(THF)(**DDQ**)}$_2$] (magenta), [{K(18-crown-6) (**DDQ**)}$_2$] (blue), ([{K(dibenzo-18-crown-6)(**DDQ**)}$_2$] (yellow), [{Na(15-crown-5)(**DDQ**)}$_2$] (red), ($Na^+$(cryptand))$_2$[**DDQ**$_2$] (olive), ($Et_4N$)$_2$[**DDQ**$_2$] (black). For comparison, black dashed line shows spectrum of the [{Na(15-crown-5)(**DDQ**)}$_2$] dimer in dichloromethane solution.

Chart S1. Atomic charges of **DDQ**$^{-\bullet}$ for the electrostatics energies and forces computations.

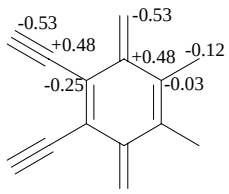
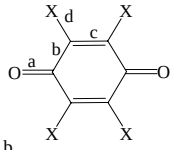


**Table S1**. Geometric characteristics of the *p*-benzoquinone moieties (in Å) [a].




| Counter-ion | Type[b] | a | b | c |
|---|---|---|---|---|
| Dichlorodicyano-p-benzoquinone | | | | |
| | N [c] | 1.214 | 1.497 | |
| | | 1.219 | 1.487 | 1.354 |
| | | | 1.499 | 1.354 |
| | | | 1.481 | |
| | | **1.217** | **1.491** | **1.354** |
| $(Fc^{*})^{+}$ [d] | SM | 1.247 | 1.454 | 1.369 |
| | | | 1.444 | 1.384 |
| | | **1.247** | **1.449** | **1.377** |
| $Na^{+}$(cryptand) | SD | 1.235 (3) | 1.453 | |
| | | | 1.469 | 1.374 |
| | | 1.244 | 1.407 | 1.398 |
| | | | 1.452 | |
| | | **1.240** | **1.445** | **1.386** |
| $K^{+}$(18-crown-6)[g] | NTD | 1.242(7) | 1.450 | |
| | | | 1.425 | 1.356 |
| | | 1.231 | 1.463 | 1.375 |
| | | | 1.468 | |
| | | **1.237** | **1.452** | **1.366** |
| $K^{+}$(dibenzo-18-crown-6) | TD | 1.249(4) | 1.472 | |
| | | | 1.461 | 1.394 |
| | | 1.241 | 1.479 | 1.354 |
| | | | 1.454 | |
| | | | 1.479 | |
| | | 1.246 | 1.448 | 1.383 |
| | | 1.243 | 1.474 | 1.354 |
| | | | 1.453 | |
| | | **1.245** | **1.465** | **1.372** |
| $Na^{+}$(15-crown-5) | TD | 1.236(7) | 1.471 | |
| | | | 1.478 | 1.357 |
| | | 1.242 | 1.454 | 1.388 |
| | | | 1.493 | |
| | | **1.239** | **1.474** | **1.372** |
| $K^{+}$(18-crown-6) | TD | | **1.470** | |
| | | | **1.472** | **1.349** |
| | | **1.231 (3)** | **1.452** | **1.381** |
| | | **1.230** | **1.454** | **1.345** |
| | | **1.231** | **1.478** | **1.385** |
| | | **1.232** | **1.469** | |
| | | | **1.450** | |
| | | | **1.450** | |
| | | **1.231** | **1.462** | **1.365** |

| Counter-ion | Type[b] | a | b | c |
|---|---|---|---|---|
| Tetrachloro-p-benzoquinone | | | | |
| - | N[e] | 1.211 | 1.489 | 1.344 |
| | | **1.211** | **1.489** | **1.344** |
| $Na^+$(cryptand) | SM | 1.252 (3) | 1.456<br>1.455<br>1.447<br>1.453 | 1.366<br>1.362 |
| | | 1.251 | | |
| | | **1.252** | **1.453** | **1.364** |
| $K^+$(18-crown-6)$(THF)_2$ | SM | 1.247 (3) | 1.451<br>1.449<br>1.454<br>1.449 | 1.369<br>1.365 |
| | | 1.251 | | |
| | | **1.249** | **1.451** | **1.367** |
| $K^+$(15-crown-5)$_2$ | SM | 1.248 (2) | 1.456<br>1.443<br>1.446<br>1.452 | 1.365<br>1.368 |
| | | 1.254 | | |
| | | **1.251** | **1.449** | **1.367** |
| $NPr_4^+$[c] | SD | 1.249 (3) | 1.454<br>1.454<br>1.456<br>1.453 | 1.362<br>1.366 |
| | | 1.252 | | |
| | | **1.251** | **1.454** | **1.364** |
| $K^+$(18-crown-6)[g] | TD | 1.247(5) | 1.454<br>1.440<br>1.477<br>1.418 | 1.337<br>1.364 |
| | | 1.266 | | |
| | | **1.256** | **1.443** | **1.351** |
| $Na^+$(15-crown-5) | TD | 1.252(2) | 1.462<br>1.434<br>1.442<br>1.466 | 1.360<br>1.356 |
| | | 1.261 | | |
| | | **1.256** | **1.451** | **1.358** |

a) Average bond length are shown in bold, and representative values of s..u. of individual bonds (one for each structure) are shown in parenthesis. b) N- neutral molecule, SM – separated monomer, SD – separated dimer, TD – tethered dimer, NTD – non-tethered dimer. c) From ref. [5]. d) From ref [19b] e) From: van Weperen K.J.; Visser, G.J. *Acta Cryst. B.* **1972,** *28,* 338**.** (CCDC refcode TCBENQ02) f) From mixed salt [{K(18-crown-6)**DDQ**$\}_2$**]** [K(18-crown-6)$(THF)_2$]$I_3$. g) See structure in Figure S2.

Table S2. Energy (in hartrees) of the $[\mathbf{DDQ_2}]^{2-}$ π-dimers with longitudinal and transversal offsets in the presence and in the absence of counter-ions [a]

| longitudinal offset | | transversal offset | |
|---|---|---|---|
| A) $[\mathbf{DDQ}_2]^{2-}$ | -2970.742351 | B) $[\mathbf{DDQ}_2]^{2-}$ | -2970.725847 |
| C) $[\mathbf{DDQ}_2]^{2-}$+ $2Na^+$ | -3295.003594 | D) [Na-**DDQ**]$_2$ | -3295.391616 |

a) From the single-point Gaussian 98 (B3LYP/6-311G*) computations[b] based on the experimental coordinates of [(Na(crp)]**DDQ** salt (A and C) and (Na(15-crown-6)**DDQ** salt (B and D) without counter-ion (A and B) and in the presence of counter-ions (C and D). [Note that the energy of $[\mathbf{DDQ_2}]^{2-}$ + $2Na^+$ aggregate was calculated (for comparison with [{**DDQ**-Na}$_2$]) in the presence of two sodium cations, which were placed at large separation ~ 10 Å from dimer).

Table S3. Coulombic forces vectors ***F*** (normalized components $F'_x$, $F'_y$ $F'_x$ and absolute values |F|, in eV $Å^{-1}$) on the anionic p-benzoquinone due to the surrounding point charges (from π-bonded anionic benzoquinone and alkali-metal cations) in comparison with the normalized components $R'_x$, $R'_y$ and $R'_z$ of the vector **R** connecting centroids of π-bonded benzoquinones)

| Multi-ion assembly | Type | \|F\| | $F'_x$ | $F'_y$ | $F'_z$ | $R'_x$ | $R'_y$ | $R'_z$ |
|---|---|---|---|---|---|---|---|---|
| $[\mathbf{DDQ_2}]^{2-}$ | SD[a] | 0.003 | -0.52 | 0.78 | 0.32 | -0.10 | -0.58 | -0.81 |
| $[\mathbf{DDQ_2}]^{2-}$ +2Na | -[a,b] | 0.003 | -0.79 | 0.61 | 0.02 | -0.10 | -0.58 | -0.81 |
| $[\mathbf{DDQ_2}]^{2-}$ +10Na | -[a,c] | 0.004 | -0.71 | 0.05 | 0.70 | -0.10 | -0.58 | -0.81 |
| [{K(18-crown-6)(THF)·**DDQ**}$_2$] | NTD | 0.046 | 0.52 | 0.80 | -0.29 | -0.05 | -0.58 | -0.81 |
| [{Na(15-crown-5)·**DDQ**}$_2$] | TD | 0.059 | -0.47 | -0.22 | -0.86 | -0.44 | -0.00 | -0.90 |

a) From salt with $[Na(cryptand)]^+$ counter-ion. b) Taking into account two $Na^+$ cations positioned closest to π-dimer. c) Taking into account ten $Na^+$ cation surrounding π-dimer.

Table S4 Crystallographic parameters and the details of the structure refinements.

| Compound | [Na(cryptand)] **DDQ** | [{Na(15-crown-5) **DDQ**}$_2$] | [{K(dibenzo-18-crown-6) **DDQ**}$_2$] $\cdot 2CH_2Cl_2$ | [{K(18-crown-6)(THF)]$\cdot$ **DDQ**}$_2$ ] [K(18-crown-6)(THF)$_2$] $I_3$ | [{K(18-crown-6) **DDQ**}$_2$] | [{Na(15-crown-5) **CA**}$_2$] | [K(18-crown-6)(THF)$_2$]**CA** | [K(15-crown-5)$_2$] **CA** |
|---|---|---|---|---|---|---|---|---|
| Empirical formula | $C_{26}H_{36}Cl_2N_4NaO_8$ | $C_{36}H_{40}Cl_4N_4Na_2O_{14}$ | $C_{58}H_{52}Cl_8K_2N_4O_{16}$ | $C_{68}H_{104}Cl_4I_3K_3N_4O_{26}$ | $C_{40}H_{48}Cl_4K_2N_4O_{16}$ | $C_{32}H_{40}Cl_8Na_2O_{14}$ | $C_{26}H_{40}Cl_4KO_{10}$ | $C_{26}H_{40}Cl_4KO_{12}$ |
| M | 626.48 | 940.50 | 1422.84 | 2033.35 | 1060.82 | 978.22 | 693.48 | 725.48 |
| Space group | P-1 | $P2_1/n$ | $P2_1/n$ | P-1 | P-1 | $P2_1/n$ | P-1 | P-1 |
| a, Å | 11.725(11) | 10.475(9) | 23.161(19) | 9.801(4) | 11.798(5) | 10.4693(18) | 10.310(2) | 9.1370(9) |
| b, Å | 11.861(11) | 11.937(9) | 11.395(10) | 13.809(5) | 12.904(6) | 11.934(2) | 11.263(3) | 12.4232(14) |
| c, Å | 12.081(12) | 17.109(14) | 24.64(2) | 17.672(7) | 16.941(8) | 16.832(3) | 14.960(5) | 15.7716(17) |
| $\alpha$, ° | 73.66(9) | 90 | 90 | 107.006(7) | 81.106(9) | 90 | 100.809(19) | 83.702(2) |
| $\beta$, ° | 68.33(7) | 102.43(2) | 104.468(19) | 95.915(7) | 74.123(9) | 103.684(17) | 95.31(2) | 74.859(2) |
| $\gamma$, ° | 86.56(8) | 90 | 90 | 105.038(7) | 79.622(9) | 90 | 108.649(16) | 73.018(3) |
| V, $Å^3$ | 1497(3) | 2089(3) | 6297(9) | 2167.0(15) | 2425.0(19) | 2043.2(6) | 1594.9(8) | 1651.7(3) |
| Z | 2 | 2 | 4 | 1 | 2 | 2 | 2 | 2 |
| F(000) | 658 | 972 | 2920 | 1032 | 1100 | 1004 | 726 | 758 |
| $\rho$, $g/cm^3$ | 1.390 | 1.495 | 1.501 | 1.558 | 1.453 | 1.590 | 1.444 | 1.459 |
| Refls | 22900 | 12675 | 35701 | 28225 | 30079 | 31022 | 24637 | 25360 |
| Indpndt | 8909 | 3026 | 13822 | 10440 | 14042 | 6294 | 9527 | 9727 |
| Obsd [I>2$\sigma$(I)] | 3947 | 1599 | 5097 | 4542 | 7316 | 3374 | 5066 | 7577 |
| $R_1$ | 0.0602 | 0.0652 | 0.0460 | 0.0574 | 0.0668 | 0.0387 | 0.0517 | 0.0470 |
| $wR_2$ | 0.1274 | 0.1410 | 0.0831 | 0.1143 | 0.1588 | 0.0654 | 0.1090 | 0.1307 |
| GooF | 0.826 | 0.992 | 0.804 | 0.949 | 1.001 | 0.804 | 0.853 | 1.015 |