# Visualization and Quantitation of Electronic Communication Pathways in a Series of Redox-Active Pillar[6]arene-Based Macrocycles

Mehdi Rashvand Avei, Sedigheh Etezadi, Burjor Captain and Angel E. Kaifer*

Department of Chemistry, University of Miami, Coral Gables, FL 33124, U.S.A.

akaifer@miami.edu

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Supplementary Figure 45. ESI mass spectrum of P4Q-A. The main peak at m/z 859.27 corresponds to M+Na⁺.
Supplementary Figure 46. ESI mass spectrum of P4Q-B. The main peak at m/z 859.27 corresponds to M+Na⁺.
**Supplementary Table 1.** The root mean square deviation (RMSD) and the maximum deviation ($D_{\text{max}}$) in Å obtained from overlaying of the optimized structures of pillararene compounds in Figures 3 & 4 onto their X-ray structures.

| Compound | RMSD (Å) | $D_{\text{max}}$ (Å) | Ref. |
|----------|---------|-----------------|-----|
| **Supplementary Figure 26** | | | |
| P5A      | 0.3311  | 1.8608          | 1   |
| P1Q      | 0.1724  | 0.5222          | 2   |
| P3Q      | 0.1848  | 0.6028          | 3   |
| **Supplementary Figure 27** | | | |
| P6A      | 0.1528  | 0.4196          | 4   |
| P1Q      | 0.5328  | 2.6140          | This work |
| P3Q-A    | 0.3935  | 1.2140          | This work |

**Supplementary Table 2.** CIV values (in electron/bohr) for oxidized derivatives of P'5A and P6A compounds.

| Compound | Critical Iso-surface Value (CIV) |
|----------|----------------------------------|
|          | Through-bond | Through-space |
| **1,4-DimethoxybenzenePillar(5)arene** | | |
| P'5A     | 0.033         | 0.025         |
| P'1Q     | 0.033         | 0.025         |
| P'2Q     | 0.033         | 0.025         |
| P'3Q     | 0.033         | 0.026         |
| P'4Q     | 0.032         | 0.026         |
| P'5Q     | 0.033         | 0.025         |
| **1,4-DiethoxybenzenePillar(6)arene** | | |
| P6A      | 0.033         | 0.019 — 0.028 |
| P1Q      | 0.034         | 0.021 — 0.027 |
| P2Q-A    | 0.033         | 0.022 — 0.029 |
| P2Q-B    | 0.033         | 0.020 — 0.029 |
| P3Q-A    | 0.033         | 0.023 — 0.029 |
| P3Q-B    | 0.031         | 0.020 — 0.029 |
| P4Q-A    | 0.034         | 0.022 — 0.028 |
| P4Q-B    | 0.034         | 0.024 — 0.026 |
Supplementary Table 3. UV-vis absorption data of 1,4-diethoxybenzene, 1,4-dimethoxybenzene, and oxidized derivatives of pillar[6]arene, and pillar[5]arene.

| Compound                        | $\lambda_{\text{max}}$ (nm) |
|---------------------------------|-----------------------------|
| 1,4-Diethoxybenzene (1,4-DEB)   | 292                         |
| P6A                             | 294                         |
| P1Q                             | 294                         |
| P2Q-A                           | 294                         |
| P2Q-B                           | 292                         |
| P3Q-A                           | 292                         |
| P3Q-B                           | 292                         |
| P4Q-A                           | 292                         |
| P4Q-B                           | 292                         |
| 1,4-dimethoxybenzene (1,4-DMB)  | 292                         |
| P'5A                            | 295                         |

Supplementary Table 4. The number of aromatic-quinone proximities and the structural parameters of the studied macrocycles.

| Compound | Sum of interior angles (in degree) | Angle strain (in degree) | The number of aromatic-quinone proximities |
|----------|-----------------------------------|--------------------------|------------------------------------------|
| P'5A     | 556.5                             | -16.5                    | 0                                        |
| P'1Q     | 554.4                             | -14.4                    | 2                                        |
| P'2Q     | 552.3                             | -12.3                    | 4                                        |
| P'3Q     | 550.9                             | -10.9                    | 4                                        |
| P'4Q     | 550.0                             | -10                      | 2                                        |
| P'5Q     | 549.0                             | -9                       | 0                                        |
| P6A      | 684.2                             | 35.8                     | 0                                        |
| P1Q      | 682.0                             | 38                       | 2                                        |
| P2Q-A    | 679.6                             | 40.4                     | 4                                        |
| P2Q-B    | 679.7                             | 40.3                     | 4                                        |
| P3Q-A    | 677.6                             | 42.4                     | 6                                        |
| P3Q-B    | 678.0                             | 42                       | 4                                        |
| P4Q-A    | 676.2                             | 43.8                     | 4                                        |
| P4Q-B    | 676.5                             | 43.5                     | 4                                        |
| P5Q      | 675.4                             | 44.6                     | 2                                        |
| P6Q      | 674.4                             | 45.6                     | 0                                        |
Supplementary Table 5. The energies (eV) of HOMO, LUMO and LUMO-HOMO gap for different derivatives of per-methylated-pillar[5]arene and per-ethylated-pillar[6]arene.

| Compound                        | HOMO (eV) | LUMO (eV) | LUMO-HOMO gap (eV) |
|--------------------------------|-----------|-----------|--------------------|
| **1,4-DimethoxyPillar(5)arene** |           |           |                    |
| 1,4-dimethoxybenzene           | -7.10     | 0.31      | 7.41               |
| P'5A                            | -6.64     | -0.03     | 6.62               |
| P'1Q                            | -6.73     | -2.49     | 4.24               |
| P'2Q-A                          | -6.89     | -2.54     | 4.35               |
| P'2Q-B                          | -6.80     | -2.71     | 4.09               |
| P'3Q-A                          | -7.06     | -2.74     | 4.32               |
| P'3Q-B                          | -6.91     | -2.83     | 4.08               |
| P'4Q                            | -7.09     | -2.90     | 4.20               |
| P'5Q                            | -9.08     | -2.94     | 6.14               |
| p-Benzoquinone                  | -9.52     | -2.72     | 6.80               |
| **1,4-DiethoxyPillar(6)arene**  |           |           |                    |
| 1,4-diethoxybenzene             | -7.96     | 0.29      | 8.24               |
| P6A                             | -6.65     | 0.02      | 6.66               |
| P1Q                             | -6.70     | -2.48     | 4.22               |
| P2Q-A                           | -6.85     | -2.50     | 4.35               |
| P2Q-B                           | -6.78     | -2.51     | 4.26               |
| P2Q-C                           | -6.73     | -2.68     | 4.05               |
| P3Q-A                           | -7.01     | -2.54     | 4.48               |
| P3Q-B                           | -6.88     | -2.70     | 4.17               |
| P3Q-C                           | -6.79     | -2.79     | 4.00               |
| P4Q-A                           | -7.05     | -2.72     | 4.33               |
| P4Q-B                           | -7.03     | -2.81     | 4.22               |
| P4Q-C                           | -6.89     | -2.86     | 4.03               |
| P5Q                             | -7.06     | -2.90     | 4.17               |
| P6Q                             | -9.05     | -2.94     | 6.11               |
| p-Benzoquinone                  | -9.52     | -2.72     | 6.80               |
Supplementary Table 6. Crystallographic Data for Compounds P1Q, P2Q-A and P3Q-A.

|                          | P1Q                              | P2Q-A                           | P3Q-A                           |
|--------------------------|----------------------------------|---------------------------------|---------------------------------|
| Empirical formula        | C$_{62}$H$_{74}$O$_{12}$•CHCl$_3$ | C$_{62}$H$_{74}$O$_{12}$•3 C$_6$H$_6$ | C$_{54}$H$_{54}$O$_{12}$•1.5 CHCl$_3$ |
| Formula weight           | 1262.73                          | 1187.41                         | 1074.02                         |
| Crystal system           | Triclinic                        | Triclinic                       | Trigonal                        |
| Lattice parameters       |                                  |                                 |                                 |
| $a$ (Å)                  | 13.2765(7)                       | 10.6523(14)                     | 13.6522(5)                      |
| $b$ (Å)                  | 13.6027(7)                       | 13.3466(18)                     | 13.6522(5)                      |
| $c$ (Å)                  | 19.7254(11)                      | 13.5912(18)                     | 53.130(2)                       |
| $\alpha$ (deg)          | 82.139(1)                        | 109.800(2)                      | 90                              |
| $\beta$ (deg)           | 84.547(1)                        | 100.880(2)                      | 90                              |
| $\gamma$ (deg)          | 77.580(1)                        | 111.292(2)                      | 120                             |
| V (Å$^3$)                | 3438.3(3)                        | 1583.2(4)                       | 8575.8(7)                       |
| Space group              | $P \bar{1}$ (# 2)               | $P \bar{1}$ (# 2)              | $R 3c$ (# 161)                  |
| Z value                  | 2                                | 1                               | 6                               |
| $\rho_{calc}$ (g/cm$^3$) | 1.220                            | 1.245                           | 1.248                           |
| $\mu$ (Mo Kα) (mm$^{-1}$)| 0.196                            | 0.083                           | 0.288                           |
| Temperature (K)          | 100                              | 100                             | 294                             |
| 2$\Theta_{max}$ (°)     | 50.00                            | 50.00                           | 56.00                           |
| No. Obs. ($I > 2\sigma(I)$)| 8168                           | 4053                            | 4195                            |
| No. Parameters           | 764                              | 401                             | 237                             |
| Goodness of fit          | 1.014                            | 1.016                           | 1.164                           |
| Max. shift in cycle      | 0.001                            | 0.000                           | 0.001                           |
| Residuals*: R1; wR2      | 0.1086; 0.2963                    | 0.0502; 0.1256                  | 0.0543; 0.1571                  |
| Absorption Correction,   | Multi-scan                       | Multi-scan                      | Multi-scan                      |
| Max/min                  | 0.7457/0.6787                    | 0.7457/0.5988                   | 0.7461/0.6811                   |
| Largest peak in Final Diff. Map (e$^-$/Å$^3$) | 2.065 | 0.768 | 0.860 |

*R1 = \sum_{hkl}(|F_{obs}| - |F_{calc}|)/\sum_{hkl}|F_{obs}|; wR2 = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}^2]^{1/2}; w = 1/\sigma^2(F_{obs}); GOF = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/[n_{data} - n_{param}]^{1/2}.}
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