Supplementary Information

The impact of cation-π, anion-π, and CH-π interactions on excited state intramolecular proton transfer of 1,4-dihydroxyanthraquinone

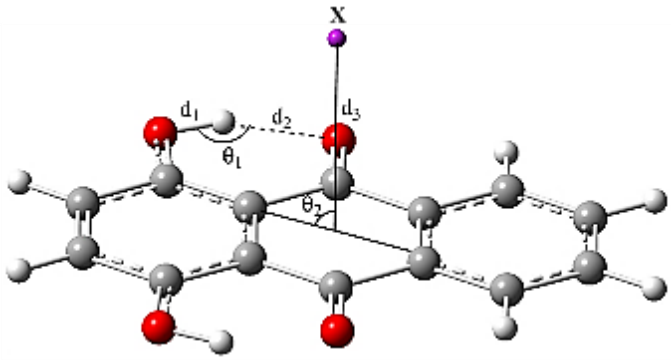
Asiyeh Shahraki, Ali Ebrahimi*, Shiva Rezazadeh, Roya Behazin

Department of Chemistry, Computational Quantum Chemistry Laboratory, University of Sistan and Baluchestan, P.O. XZBox 98135-674, Zahedan, Iran

* Corresponding author E-mail: ebrahimi@chem.usb.ac.ir (A. Ebrahimi)

Fax: +98-54-33446565

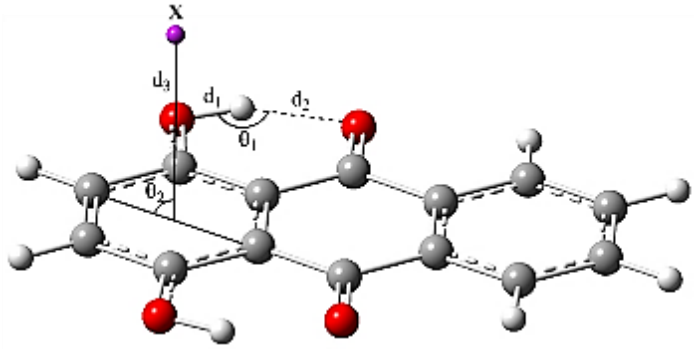
Table S1. The important geometrical parameters for the complexes of type b in the S_0 and S_1 states



X	d_1/Å	d_2/Å	d_3/Å	θ_1/°	θ_2/°
Q	0.978 (0.979) **1.017 (1.028)**	1.732 (1.734) **1.554 (1.516)**		143.95 (143.77) **151.76 (153.08)**	
Mg^{2+}	0.981 (0.979) **(1.026)**	1.826 (1.735) **(1.523)**	1.831 (3.263) **(3.259)**	138.29 (143.70) **(152.84)**	89.21 (90.92) **(91.61)**
Ca^{2+}	0.982 (0.979) **(1.023)**	1.792 (1.733) **(1.561)**	2.248 (3.253) **(3.257)**	139.06 (143.70) **(151.32)**	88.98 (90.43) **(89.67)**
F^-	0.977 (0.980) **(1.028)**	1.732 (1.735) **(1.514)**	2.343 (2.971) **(3.291)**	146.44 (143.86) **(153.19)**	109.83 (92.01) **(88.18)**
Cl^-	0.981 (0.978) **(1.015)**	1.695 (1.740) **(1.553)**	3.009 (3.144) **(3.482)**	146.55 (143.74) **(152.28)**	102.28 (95.23) **(79.21)**
Br^-	0.979 (0.979) **(0.995)**	1.727 (1.733) **(1.614)**	3.180 (3.237) **(3.048)**	144.97 (144.16) **(150.91)**	82.41 (92.00) **(105.52)**

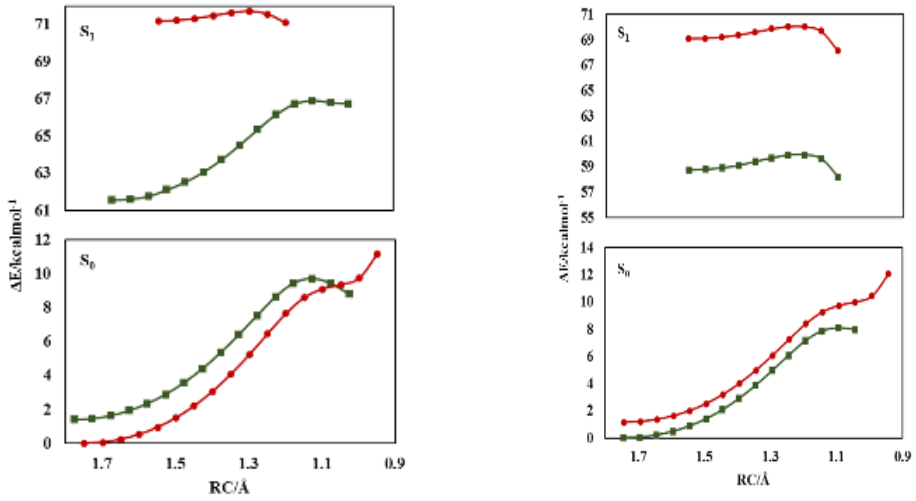
The bold values correspond to the S_1 state of complexes. The data in parentheses calculated in the solution media.

Table S2. The important geometrical parameters for the complexes of type c in the S_0 and S_1 states

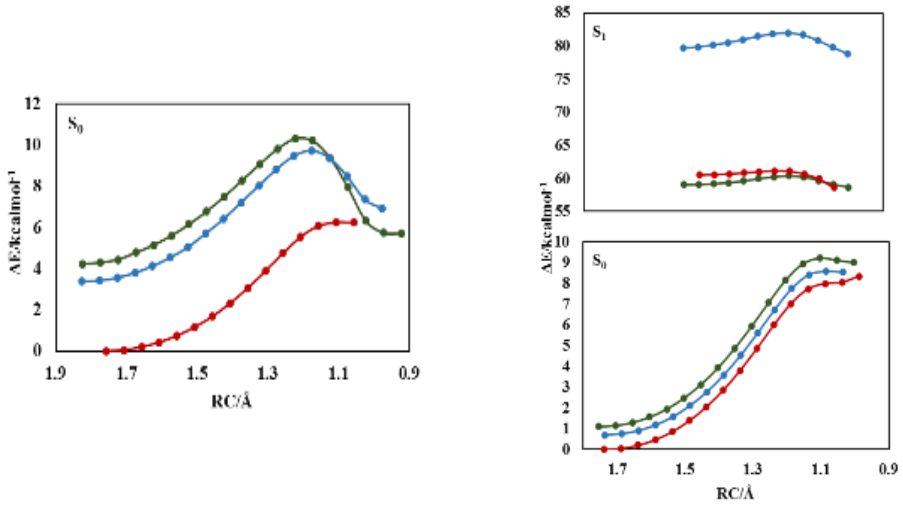


X	d_1/Å	d_2/Å	d_3/Å	θ_1/°	θ_2/°
Q	0.978 (0.979) **1.017 (1.028)**	1.732 (1.734) **1.554 (1.516)**		143.95 (143.77) **151.76 (153.08)**	
Na^+	0.980 (0.979) **1.037 (1.027)**	1.748 (1.746) **1.527 (1.548)**	2.379 (2.587) **2.477 (3.406)**	141.72 (142.89) **151.14 (151.55)**	89.27 (89.13) **83.32 (57.84)**
K^+	0.979 (0.979) **1.030 (1.027)**	1.748 (1.743) **1.544 (1.550)**	2.850 (2.975) **2.936 (3.826)**	141.97 (143.07) **150.74 (151.46)**	89.84 (87.60) **87.68 (61.53)**
Mg^{2+}	0.986 (0.979) **(1.029)**	1.757 (1.737) **(1.512)**	1.973 (3.260) **(3.272)**	139.10 (143.57) **(153.22)**	86.89 (89.51) **(89.40)**
Ca^{2+}	0.983 (0.979) **(1.024)**	1.759 (1.734) **(1.557)**	2.320 (3.276) **(3.286)**	139.36 (143.75) **(151.49)**	90.20 (90.72) **(90.58)**
F^-	0.994 (0.979) **(1.027)**	1.668 (1.734) **(1.516)**	2.345 (3.333) **(3.303)**	150.70 (143.79) **(153.16)**	71.63 (90.44) **(94.49)**
Cl^-	**(1.018)**	**(1.574)**	**(3.260)**	**(151.21)**	**(92.01)**
Br^-	**(1.010)**	**(1.557)**	**(3.200)**	**(152.65)**	**(98.42)**

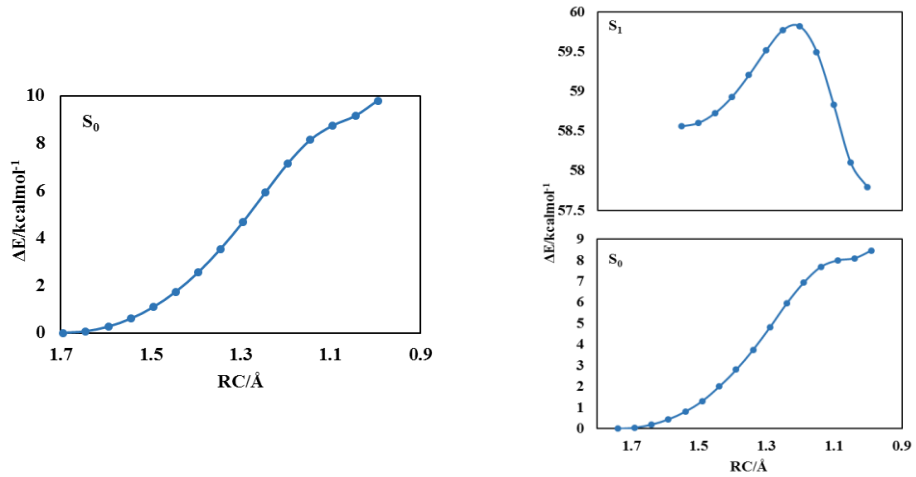
The bold values correspond to the S_1 state of complexes. The data in parentheses calculated in the solution media.



Q-K^+

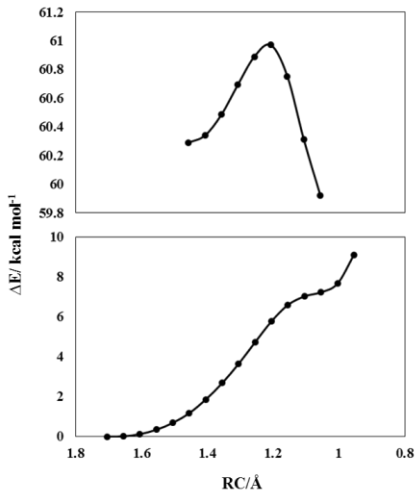


Q-Mg^{2+}

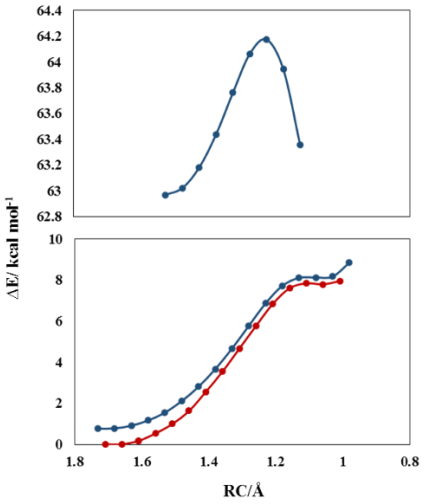


Q-Cl^-

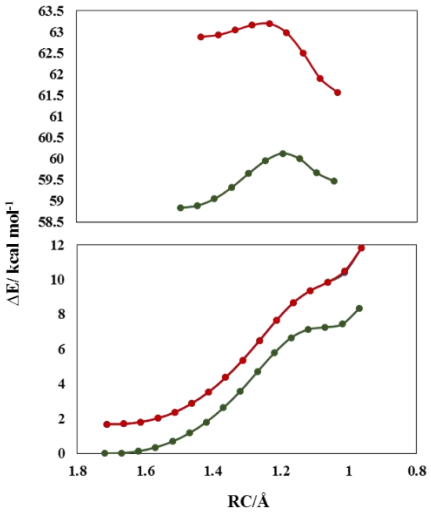
Figure S1. The potential energy curves of S_0 and S_1 states in the gas phase (left panel) and solution media (right panel) calculated at the M06-2X/6-311++G(d,p) level. The green, blue, and red curves correspond to the complexes of types a, b, and c, respectively.



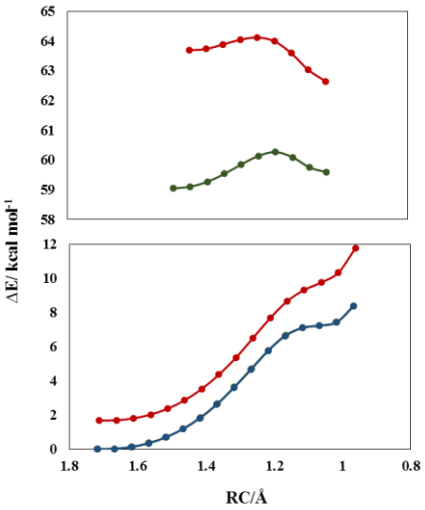
Q



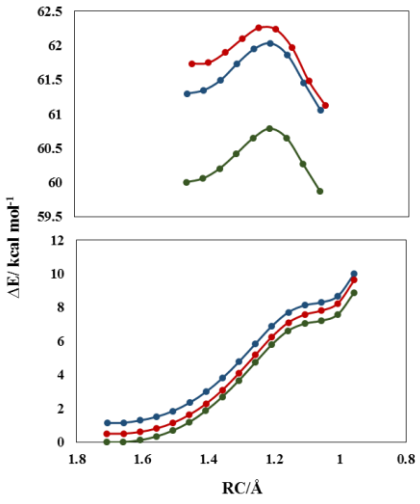
Q-CH_3F



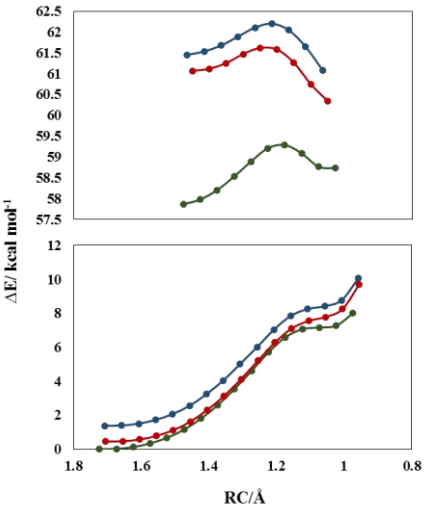
Q-Na^+



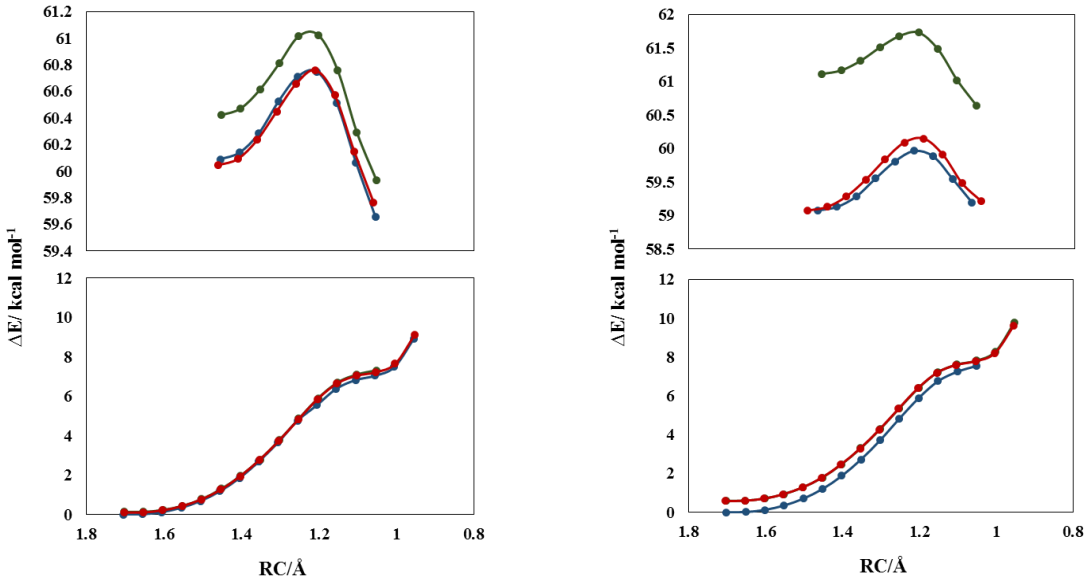
Q-K^+



Q-Ca^{2+}

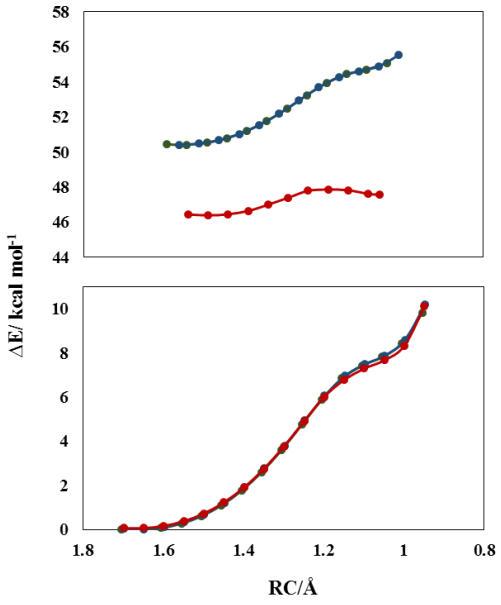


Q-Mg^{2+}



Q-F⁻

Q-Cl⁻



Q-Br⁻

Figure S2. The potential energy curves of S_0 and S_1 states in the DMSO solvent calculated at the M06-2X/6-311++G(d,p) level. The green, blue, and red curves correspond to the complexes of types a, b, and c, respectively.

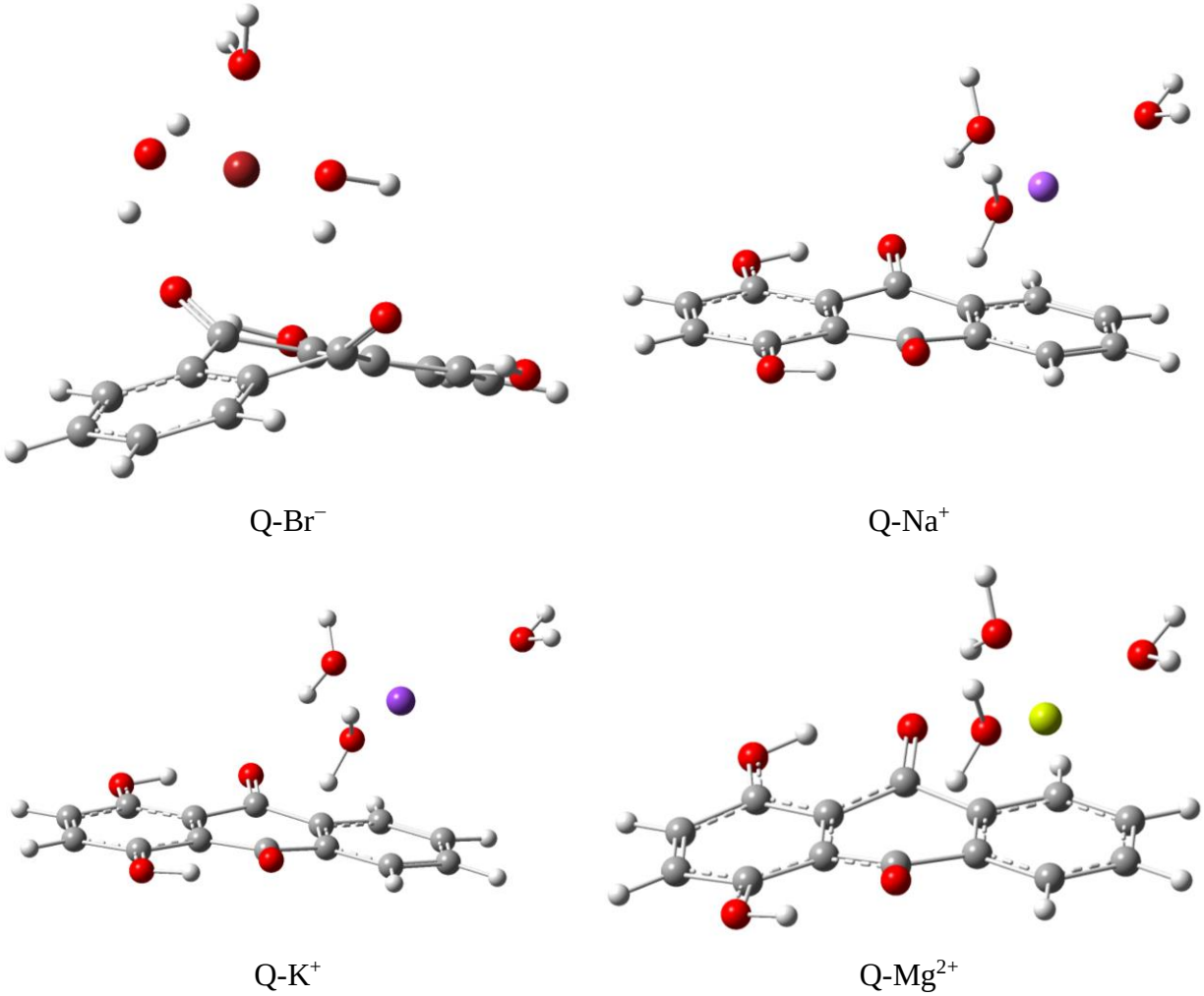
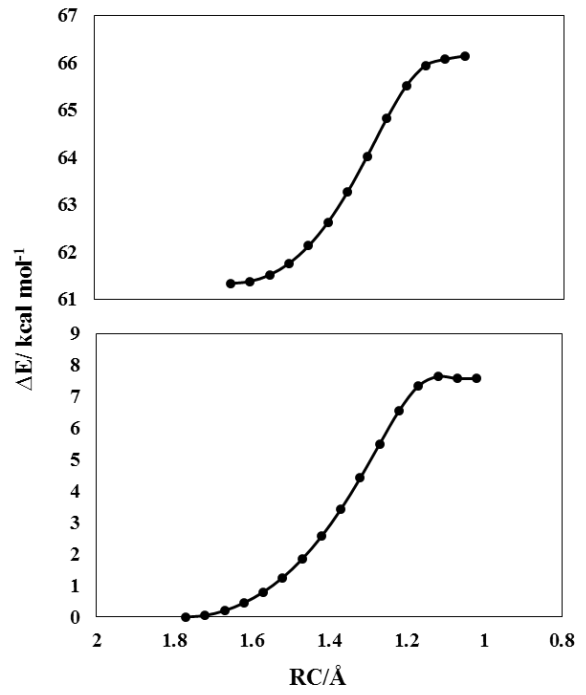
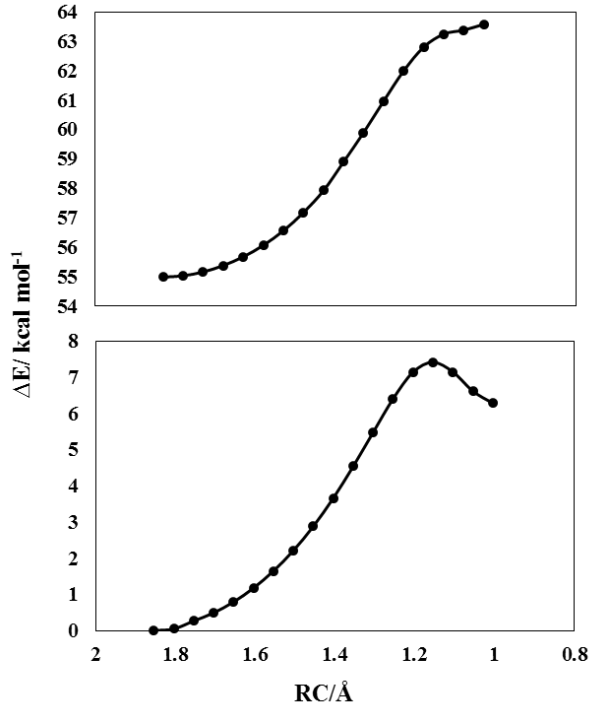


Figure S3. The optimized structures of some complexes in the present of explicit water molecules calculated at the M06-2X/6-311++G(d,p) level.

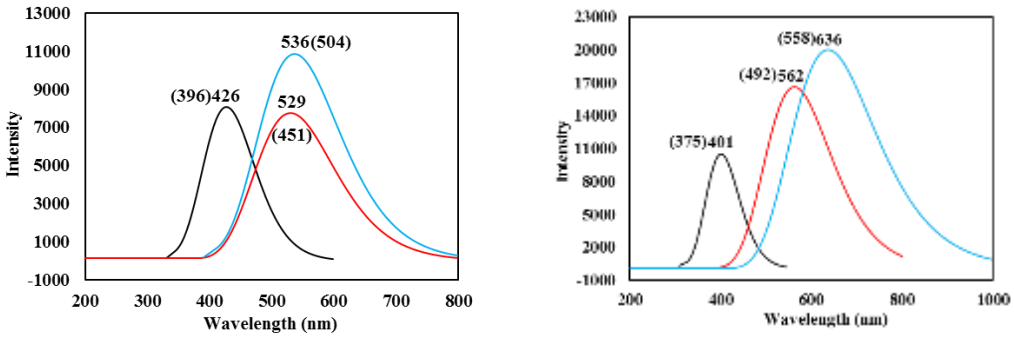


Q-K^+

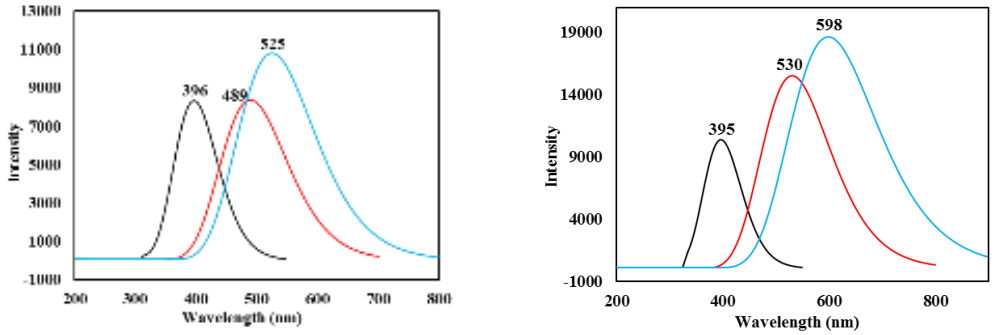


Q-Ca^{2+}

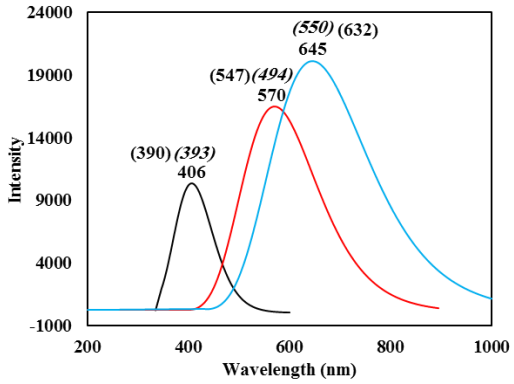
Figure S4. The potential energy curves of S_0 and S_1 states for some complexes in the present of explicit water molecules calculated at the M06-2X/6-311++G(d,p) level.



Q-K^+



Q-CF_3H



Q-Mg^{2+}

Figure S5. The absorption and fluorescence spectra calculated at the TDDFT/M06-2X/6-311++G(d,p) theoretical level. The black, red, and blue lines represent the absorption, S_1-N, and S_1-T fluorescence emission, respectively. The italicized values and those are in the parenthesis correspond to the complexes of types b and c, respectively.