Supplementary Materials

Solvent Effects and Metal Ions Recognition in Some Azulenyl-Vinyl-Oxazolones

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Basic properties for ligands and characterization by elemental analysis, UV-Vis, ^{1}H NMR, ^{13}C-NMR, IR, MS

4-(Azulen-1-ylmethylene)-2-phenyloxazol-5(4H)-one, (O1). Brown reddish (brick) crystals, m.p. 258–261 ◦C. UV-Vis (MeOH), λ(log ε): 230 (4.53), 282 (4.30), 293 (4.28), 312 (4.17), 317 sh (4.17), 328 (4.17), 410 (4.15), 468 (4.45). ^{1}H-NMR (300 MHz, CDCl3, 20 ◦C): 7.44 (t, 3 J = 9.8 Hz, 1 H, 5-H), 7.49 (t, 3 J = 9.8 Hz, 1 H, 7-H), 7.52–7.60 (m, 4 H, 3-H, 30 -H, 5 0 -H, 40 -H), 7.78 (t, 3 J = 9.8 Hz, 1 H, 6-H), 7.94 (s, 1 H, CH=), 8.22 (dd, 3 J = 7.6 Hz, 4 J = 1.0 Hz, 2 H, 20 -H, 60 -H), 8.41 (d, 3 J = 9.5 Hz, 1 H, 4-H), 8.72 (d, 3 J = 9.8 Hz, 1 H, 8-H), 9.30 (d, 3 J = 4.3 Hz, 1 H, 2-H) ppm. ^{13}C-NMR (75.47 MHz, CDCl3, 20 ◦C): 122.2, 123.4, 124.3, 126.4, 126.9, 127.8, 128.0, 128.8, 129.1, 132.4, 134.0, 137.9, 139.4, 141.0, 141.9, 145.5, 160.7, 168.6 ppm. IR (neat): 3492 w, 3063 w, 3024 w, 2620 w, 2448 w, 2187 w, 1817 w, 1754 vs, 1626 vs, 1580 s, 1485 s, 1446 s, 1387 s, 1284 s, 1173 s, 1043 m, 1012 m, 969 s, 847 s, 770 s,737 s, 687 s cm^{-1} . MS (+ESI): 300 [M+1]. Calcd. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.21; H, 4.39; N, 4.66.

2-Phenyl-4-((4,6,8-trimethylazulen-1-yl)methylene)oxazol-5(4H)-one, (O2). Dark violet crystals, m.p. 214–216 °C. UV-Vis (MeOH), λ(log ε): 243 (4.43), 295 sh (3.97), 329 (4.14), 404 sh (3.92), 486 (4.40). ^{1}H-NMR (300 MHz, $CDCl_3$, 20 °C): 2.63 (s, 3 H, Me), 2.89 (s, 3 H, Me), 3.19 (s, 3 H, Me), 7.25 (s, 1 H, 5-H), 7.26 (s, 1 H, 7-H), 7.46 (d, ^{3}J = 4.7 Hz, 1 H, 3-H), 8.17 (dd, ^{3}J = 7.9 Hz, ^{4}J = 1.5 Hz, 2 H, 2′-H, 6-H), 7.48–7.55 (m, 3 H, 3′-H, 4′-H, 5′-H), 8.25 (s, 1 H, CH=), 9.16 (d, ^{3}J = 4.7 Hz, 1 H, 2-H) ppm. ^{13}C-NMR (75.47, MHz, $CDCl_3$, 20 °C): 26.0, 28.4, 30.1, 119.8, 125.6, 126.6, 127.7, 128.8, 129.1, 129.5, 132.0, 132.1, 133.8, 138.1, 139.9, 142.6, 146.9, 148.1, 148.2, 160.3, 169.0 ppm. IR (neat): 3103 w, 2918 vs, 2855 s, 2175 w, 1723 vs, 1612 s, 1571 s, 1490 s, 1517 s, 1403 s, 1318 s, 1265 vs, 1152 s, 1020 s, 839 m, 698 m cm^{-1}. MS (+ESI): 342 [M+1]. Calcd. for $C_{23}H_{19}NO_2$: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.90; H, 5.60; N, 4.13.

4-((5-isopropyl-3,8-dimethylazulen-1-yl)methylene)-2-phenyloxazol-5(4H)-one, (O3). Dark green crystals, m.p.166–168 ◦C. UV-Vis (MeOH), λ(log ε): 233 sh (4.45), 244 (4.47), 315 (4.07), 363 (3.93), 510 (4.53). ^{1}H-NMR (300 MHz, CDCl3, 20 ◦C): 1.39 (d, 3 J = 6.9 Hz, 6 H, CHMe), 2.67 (s, 3 H, Me3), 3.12 (sept, 3 J = 6.9 Hz, 1 H, CHMe2), 3.18 (s, 3 H, Me8), 7.26 (d, 3 J = 10.8 Hz, 1 H, 6-H), 7.47–7.55 (m, 4 H, 7-H, 30 -H, 40 -H, 50 -H), 8.17 (d, 4 J = 1.7 Hz, 1 H, 4-H), 8.31 (dd, 3 J = 7.3 Hz, 4 J = 1.7 Hz, 2 H, 20 -H, 60 -H), 8.24 (s, 1 H, CH=), 9.13 (s, 1 H, 2-H) ppm. ^{13}C-NMR (75.47, MHz, CDCl3, 20 ◦C): 13.3, 24.4, 29.1, 38.0, 123.2, 127.2, 127.6, 127.9, 128.8, 129.7, 133.0, 134.5, 136.4, 140.0, 141.8, 144.1, 147.0, 147.2, 159.9, 169.1 ppm. IR (neat): 3063 w, 2956 m, 2915 m, 2068 w, 1758 vs, 1615 vs, 1582 s, 1525 s, 1422 s, 1342 s, 1324 s, 1151 s, 1094 br, 971 m, 864 m, 684 s cm^{-1} . MS (+ESI): 370 [M+1]. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found: C, 81.25; H, 6.27; N, 3.80.

4-(azulen-1-ylmethylene)-2-(4-nitrophenyl)oxazol-5(4H)-one, (**O4**) Dark green crystals, m.p. 295–297 ◦C. UV-Vis (MeOH), λ(log ε): 233 (4.15), 246 sh (4.12), 325 (4.07), 397 (3.99), 507 (3.75). ^{1}H-NMR (600 MHz, CDCl3, 20 ◦C): 7.50 (t, 3 J = 9.8 Hz, 1H, 5-H), 7.56 (t, 3 J = 9.8 Hz, 1H, 7-H), 7.60 (d, 3 J = 4.3 Hz, 1H, 3-H), 7.83 (t, 3 J = 9.8 Hz, 1H, 6-H), 8.03 (s, 1H, CH=), 8.35 (dd, 3 J = 7.6 Hz, 4 J = 1.0 Hz, 2 H, 20 -H, 60 -H), 8.38 (dd, 3 J = 7.6 Hz, 4 J = 1.0 Hz, 2 H, 30 -H, 50 -H), 8.45 (d, 3 J = 9.5 Hz, 1H, 4-H), 8.75 (d, 3 J = 9.8 Hz, 1H, 8-H), 9.26 (d, 3 J = 4.3 Hz, 1H, 2-H) ppm. ^{13}C-NMR (150 MHz, CDCl3, 20 ◦C): 122.9, 124.1, 124.3, 125.7, 127.8, 128.3, 128.4, 128.7, 132.1, 134.2, 138.3, 139.8, 141.2, 142.9, 146.3, 149.7, 158.3, 167.8 ppm. IR (neat): 3083 w, 2918 w, 2610 w, 1767 s, 1723 m, 1632 s, 1585 s, 1401 m, 1317 vs, 1286 s, 1170 m, 1094 m, 848 m, 605 m cm−1 . MS (+ESI): 345 [M+1]. Calcd. for $C_{20}H_{12}N_2O_4$: C, 69.76; H, 3.51; N, 8.14. Found: C, 69.79; H, 3.50; N, 8.11.

2-(4-Nitrophenyl)-4-((4,6,8-trimethylazulen-1-yl)methylene)oxazol-5(4H)-one, (**O5**). Dark green crystals, m.p. 269–270 ◦C. UV-Vis (MeOH), λ(log ε): 236 (4.06), 257 (4.03), 333 (3.93), 405 (3.70), 521 (3.93). ^{1}H-NMR (300 MHz, CDCl3, 20 ◦C): 2.67 (s, 3 H, Me6), 2.92 (s, 3 H, Me4), 3.22 (s, 3 H, Me8), 7.34 (s, 2 H, 5-H, 7-H), 7.48 (d, 3 J = 4.7 Hz, 1 H, 3-H), 8.37 (s, 1H, CH=), 8.36–8.29 (m, 5 H, 20 -H, 60 -H, 30 -H, 50 -H), 9.16 (d, 3 J = 4.5 Hz, 1 H, 2-H) ppm. ^{13}C-NMR (75.47, MHz, CDCl3, 20 ◦C): 26.1, 28.4, 30.2, 120.5, 124.1, 125.8, 126.8, 128.2, 131.3, 132.2, 133.2, 134.8, 139.1, 140.1, 143.6, 147.5, 148.6, 148.7, 157.8, 168.2 ppm. IR (neat): 3094 w, 2914 w, 1786 w, 1748 s, 1619 m, 1585 s, 1508 s, 1411 w, 1321 vs, 1219 m, 1166 m, 1091 m, 855 s, 713 s cm^{-1} . MS (+ESI): 387 [M+1]. Calcd. for $C_{23}H_{18}N_2O_4$: C, 71.49; H, 4.70; N, 7.25. Found: C, 71.47; H, 4.71; N, 7.21.

4-((5-Isopropyl-3,8-dimethylazulen-1-yl)methylene)-2-(4-nitrophenyl)oxazol-5(4H)-one, (**O6**). Dark green crystals, m.p. 261–263 ◦C. UV-Vis (MeOH), λ(log ε): 246 (4.27), 334 (4.13), 423 (3.98), 546 (4.19). ^{1}H-NMR (300 MHz, CDCl3, 20 ◦C): 1.42 (d, 3 J = 6.8 Hz, 6 H, MeCH), 2.69 (s, 3 H, Me3), 3.16 (sept, 3 J = 6.8 Hz, 1 H, CHMe2), 3.21 (s, 3 H, Me8), 7.36 (dAB, 3 J = 10.3 Hz, 5-H), 7.57 (dAB, d, 3 J = 10.3 Hz, 4 J = 1.0 Hz, 1 H, 6-H), 8.21 (d, 4 J = 1.0 Hz, 1 H, 4-H), 8.30 (d, 3 J = 9.0 Hz, 2 H, 20 ,60 -Ph), 8.36 (d, 3 J = 9.0 Hz, 2 H, 30 ,50 -Ph), 8.33 (s, 1 H, CH=), 9.11 (s, 1 H, 2-H). ^{13}C-NMR (75.47 MHz, CDCl3, 20 ◦C): 13.3, 24.4, 29.2, 38.1, 123.5, 124.3, 126.3, 128.0, 129.9, 130.6, 132.2, 134.1, 134.8, 136.8, 141.2, 141.8, 145.1, 147.6, 148.5, 149.3, 157.2, 168.3. IR (neat): 3482 w, 3072 br, 2918 m, 2856 m, 1738 vs, 1617 s, 1579 s, 1504 vs, 1423 s, 1305 vs, 1147 s, 1086 s, 847 s, 694 m cm^{-1}. MS (+ESI): 415 [M+1]. Calcd. for $C_{25}H_{22}N_2O_4$: C, 72.45; H, 5.35; N, 6.76. Found: C, 72.49; H, 5.34; N, 6.73.

Table S1. Code and name of investigated ligands*.

R1	R2	Code	Name
H	H	**O1**	4-(azulen-1-ylmethylene)-2-phenyloxazol-5(4H)-one
4,6,8-Me$_3$	H	**O2**	2-phenyl-4-((4,6,8-trimethylazulen-1-yl)methylene)oxazol-5(4H)-one
5-iPr-3,8-Me$_2$	H	**O3**	4-((5-isopropyl-3,8-dimethylazulen-1-yl)methylene)-2-phenyloxazol-5(4H)-one
H	NO_2	**O4**	4-(azulen-1-ylmethylene)-2-(4-nitrophenyl)oxazol-5(4H)-one
4,6,8-Me$_3$	NO_2	**O5**	2-(4-nitrophenyl)-4-((4,6,8-trimethylazulen-1-yl)methylene)oxazol-5(4H)-one
5-iPr-3,8-Me$_2$	NO_2	**O6**	4-((5-isopropyl-3,8-dimethylazulen-1-yl)methylene)-2-(4-nitrophenyl)oxazol-5(4H)-one

*According to Figure 3.

Lippert–Mataga equation:

Solvent polarity function:

$$f(\varepsilon)=\frac{(\varepsilon-1)}{(2\varepsilon+1)} \quad \text{(S1)}$$

Solvent polarizability function:

$$f(n^2)=\frac{(n^2-1)}{(2n^2+1)} \quad \text{(S2)}$$

Lippert – Mataga orientation polarizability function:

$$\Delta f_{LM}= f(\varepsilon) - f(n^2) \quad \text{(S3)}$$

$$\vartheta_A-\vartheta_f=\frac{2}{hc}\left(\frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{2n^2+1}\right)\frac{\left(\mu_{E-}\mu_G\right)^2}{a^3}+k \quad \text{(S4)}$$

In the Lippert–Mataga equation, *h* is the Planck constant, *c* represents the light speed in vacuum, *a* is the radius of the cavity where the dye is allocated, νA and νF are the absorption and emission wavenumber, respectively, and *k* is a constant representing the difference between the absorption and emission wavenumbers in the vacuum.

Bakshiev equation:

$$\vartheta_A-\vartheta_f=m_1F_1(\varepsilon,n)+const$$

$$F_1(\varepsilon,n)=\left[\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right]\left(\frac{2n^2+1}{n^2+2}\right) \quad \text{(S5)}$$

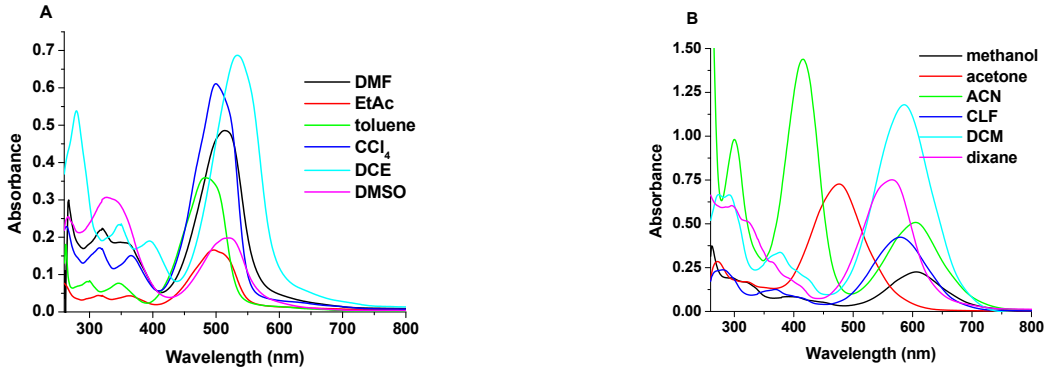


Figure S1. UV-Vis absorption spectra of azulene derivative in solvents having different polarities a) **O3**, b) **O6.**

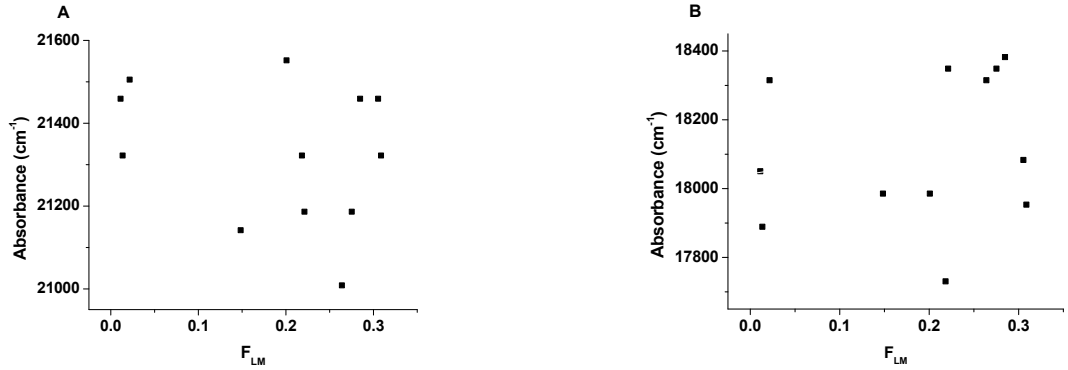
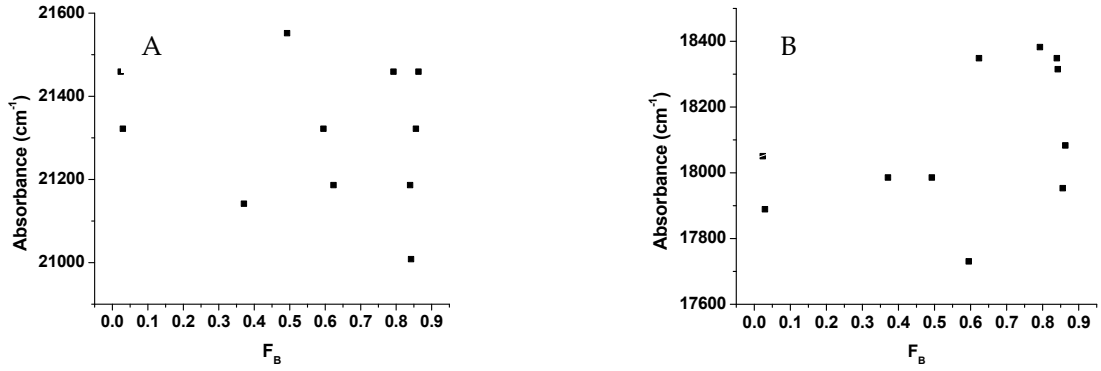


Figure S2. Lippert-Mataga solvent polarity function (F_{LM}) plots for a) **O1,** b) **O6**.



FigureS3. Bakhshiev solvent polarity function plots for a) **O1,** b) **O6**.

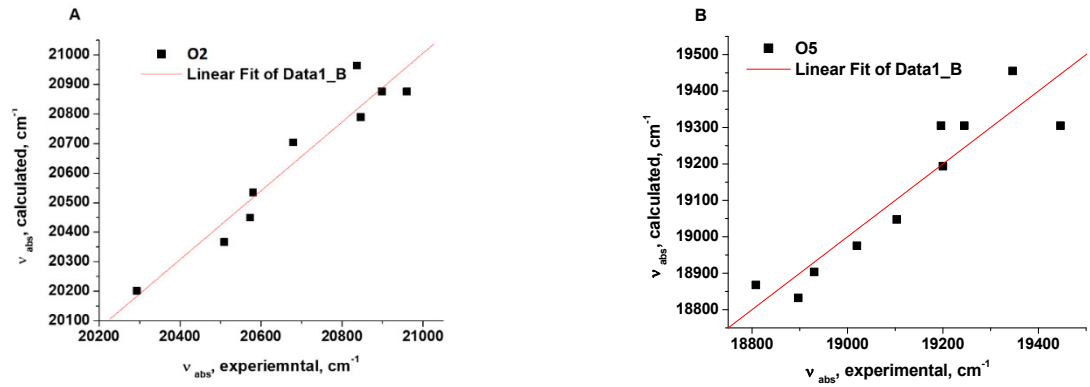


Figure S4. Linear correlation plots using equation (6) for a) **O2**, b) **O5**.

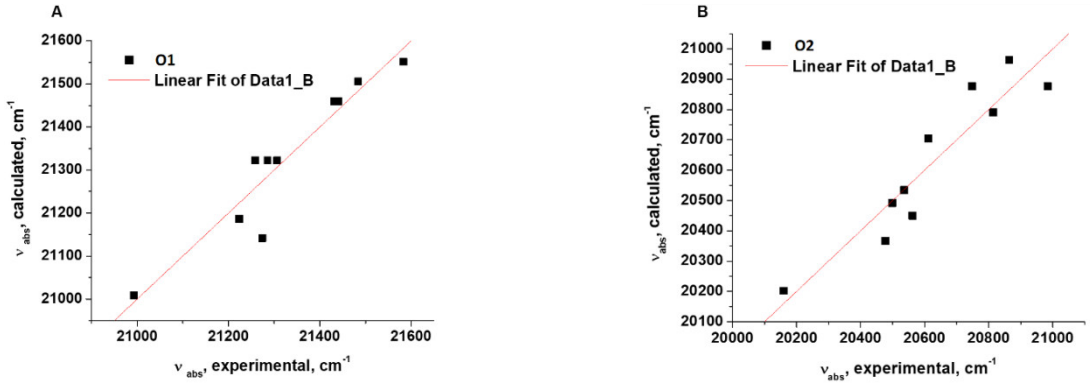


Figure S5. Linear correlation plots using equation (7) for a) **O1**, b) **O2**.

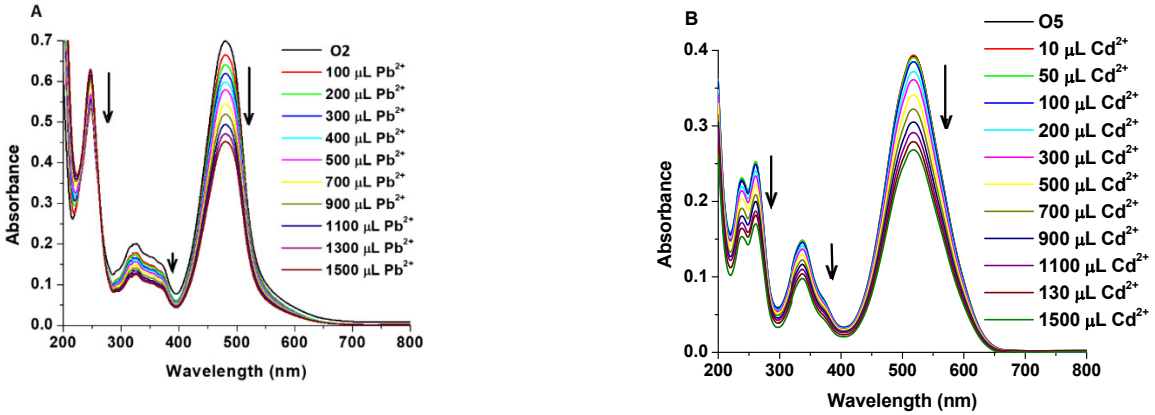


Figure S6. Changes in the UV-vis absorption spectra in acetonitrile solution upon addition of increasing amounts of a) Pb^{2+} for **O2**, b) Cu^{2+} for **O5**.

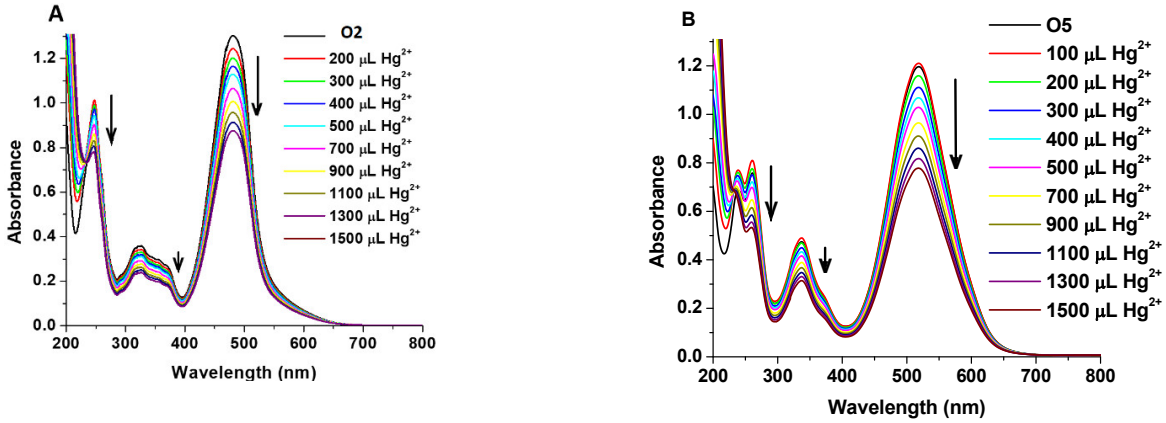


Figure S7. Changes in the UV-vis absorption spectra in acetonitrile solution upon addition of increasing amounts of Hg^{2+} a) for **O2**, b) for **O5.**