Electronic Supplementary Information

Rhenium tricarbonyl complexes of AIE active tetraarylethylene ligands: tuning luminescence properties and HSA-specific binding

Moustafa T. Gabr and F. Christopher Pigge

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, United States

chris-pigge@uiowa.edu

Contents

UV-vis absorption spectrum of 2 S3
UV-vis absorption spectrum of 3 S3
UV-vis absorption spectrum of 4 S4
UV-vis absorption spectrum of 5 S4
UV-vis absorption spectrum of 6 S5
UV-vis absorption spectrum of 7 S5
UV-vis absorption spectrum of 8 S6
UV-vis absorption spectrum of 9 S6
UV-vis absorption spectrum of 10 S7
UV-vis absorption spectrum of 11 S7
UV-vis absorption spectrum of 12 S8
UV-vis absorption spectrum of 13 S8
UV-vis absorption spectrum of 14 S9
UV-vis absorption spectrum of 15 S9
UV-vis absorption spectrum of 16 S10
AIE profile of 2 in CH3CN/H2O mixtures S10
AIE profile of 3 in CH3CN/H2O mixtures S11
AIE profile of 4 in CH3CN/H2O mixtures S11
AIE profile of 5 in CH3CN/H2O mixtures S12
Emission spectra of 6 in degassed and aerated MeCN S12
Emission spectra of 7 in degassed and aerated MeCN S13
Emission spectra of 8 in degassed and aerated MeCN S13
Emission spectra of 9 in degassed and aerated MeCN S14
Emission spectra of 10 in degassed and aerated MeCN
AIE profile of 11 in CH₃CN/PBS mixtures
AIE profile of 12 in CH₃CN/PBS mixtures
ACQ profile of 13 in CH₃CN/PBS mixtures
AIE profile of 14 in CH₃CN/PBS mixtures
ACQ profile of 15 in CH₃CN/PBS mixtures
Dynamic light scattering results of 16 in 9:1 PBS:MeCN
UV-vis absorption spectrum of 16 in MeCN and 9:1 PBS:MeCN
UV-vis absorption spectrum of 16 in 9:1 PBS:MeCN over 48 hr period
UV-vis absorption spectrum of 16 in 9:1 PBS:MeCN at pH 7.4 and 12.0
UV-vis absorption spectrum of 17
Overlay of UV-vis spectra of 16 and 17
Emission response of 5 in presence of HSA
Emission response of 11 in presence of HSA
Emission response of 12 in presence of HSA
Emission response of 13 in presence of HSA
Emission response of 14 in presence of HSA
Emission response of 15 in presence of HSA
Emission response of 16 in presence of different amino acids
Saturation binding assay of 16 towards HSA
Emission response of 16-HSA in presence of SDS
Photophysical properties of 6-16
X-ray crystallographic data for 12
References
IR spectra of 7, 8, 9, 11 and 12
NMR spectra for all new compounds
Figure S1. UV-vis absorption spectrum of 2 (CH₃CN, 25 μM).

Figure S2. UV-vis absorption spectrum of 3 (CH₃CN, 12.5 μM).
Figure S3. UV-vis absorption spectrum of 4 (CH$_3$CN, 12.5 µM).

Figure S4. UV-vis absorption spectrum of 5 (CH$_3$CN, 25 µM).
Figure S5. UV-vis absorption spectrum of 6 (CH$_3$CN, 50 µM).

Figure S6. UV-vis absorption spectrum of 7 (CH$_3$CN, 25 µM).
Figure S7. UV-vis absorption spectrum of 8 (CH$_3$CN, 12.5 µM).

Figure S8. UV-vis absorption spectrum of 9 (CH$_3$CN, 25 µM).
Figure S9. UV-vis absorption spectrum of 10 (CH$_3$CN, 12.5 µM).

Figure S10. UV-vis absorption spectrum of 11 (CH$_3$CN, 12.5 µM).
Figure S11. UV-vis absorption spectrum of 12 (CH$_3$CN, 12.5 µM).

Figure S12. UV-vis absorption spectrum of 13 (CH$_3$CN, 12.5 µM).
Figure S13. UV-vis absorption spectrum of 14 (CH₃CN, 12.5 µM).

Figure S14. UV-vis absorption spectrum of 15 (CH₃CN, 12.5 µM).
Figure S15. UV-vis absorption spectrum of 16 (CH₃CN, 12.5 µM).

Figure S16. AIE profile of 2 in CH₃CN/H₂O mixtures. λₑₓ = 318 nm, [2] = 10 µM.
**Figure S17.** AIE profile of 3 in CH$_3$CN/H$_2$O mixtures. $\lambda_{ex} = 367$ nm, [3] = 10 $\mu$M.

**Figure S18.** AIE profile of 4 in CH$_3$CN/H$_2$O mixtures. $\lambda_{ex} = 393$ nm, [4] = 10 $\mu$M.
Figure S19. AIE profile of 5 in CH$_3$CN/H$_2$O mixtures. $\lambda_{ex} = 354$ nm, $[5] = 10$ μM.

Figure S20. Emission spectra of 6 in degassed and aerated MeCN. $\lambda_{ex} = 326$ nm, $[6] = 10$ μM.
Figure S21. Emission spectra of 7 in degassed and aerated MeCN. $\lambda_{ex} = 340$ nm, $[7] = 10$ $\mu$M.

Figure S22. Emission spectra of 8 in degassed and aerated MeCN. $\lambda_{ex} = 337$ nm, $[8] = 10$ $\mu$M.
Figure S23. Emission spectra of 9 in degassed and aerated MeCN. $\lambda_{ex} = 341$ nm, [9] = 10 $\mu$M.

Figure S24. Emission spectra of 10 in degassed and aerated MeCN. $\lambda_{ex} = 394$ nm, [10] = 10 $\mu$M.
Figure S25. AIE profile of 11 in CH₃CN/PBS (pH=7.4) mixtures. $\lambda_{ex} = 334$ nm, $[11] = 10$ μM

Figure S26. AIE profile of 12 in CH₃CN/PBS (pH= 7.4) mixtures. $\lambda_{ex} = 364$ nm, $[12] = 10$ μM.
Figure S27. ACQ profile of 13 in CH$_3$CN/PBS (PH= 7.4) mixtures. $\lambda_{ex} = 447$ nm, $[13] = 10$ $\mu$M.

Figure S28. AIE profile of 14 in CH$_3$CN/PBS mixtures (PH= 7.4). $\lambda_{ex} = 419$ nm, $[14] = 10$ $\mu$M.
Figure S29. ACQ profile of 15 in CH₃CN/PBS mixtures (PH = 7.4). λ<sub>ex</sub> = 450 nm, [15] = 10 μM.

Figure S30. Dynamic light scattering results of 16 (10 μM) in 9:1 PBS:MeCN.
Figure S31. UV-vis absorption spectrum of 16 (12.5 µM) in MeCN and 9:1 PBS:MeCN.

Figure S32. UV-vis absorption spectrum of 16 (12.5 µM, 9:1 PBS:MeCN) over 48 hr period.
Figure S33. UV-vis absorption spectrum of 16 (12.5 µM, 9:1 PBS:MeCN) at pH = 7.4 and 12.0.

Figure S34. UV-vis absorption spectrum of 17 (MeCN, 25 µM).
Figure S35. Overlay of UV-vis absorption spectra of 16 (MeCN, 12.5 µM) in red and 17 (MeCN, 25 µM) in black.

Figure S36. Emission response of 5 in presence and absence of 20 µM HSA in 9:1 PBS:MeCN (PH= 7.4).  \( \lambda_{ex} = 354 \text{ nm}, \ [5] = 10 \mu\text{M} \).
**Figure S37.** Emission response of 11 in presence and absence of 20 µM HSA in 9:1 PBS:MeCN (PH=7.4). \( \lambda_{ex} = 334 \text{ nm, } [11] = 10 \mu\text{M}. \)

**Figure S38.** Emission response of 12 in presence absence of 20 µM HSA in 9:1 PBS:MeCN (PH=7.4). \( \lambda_{ex} = 364 \text{ nm, } [12] = 10 \mu\text{M}. \)
Figure S39. Emission response of 13 in presence and absence of 20 μM HSA in 9:1 PBS:MeCN (PH=7.4). \( \lambda_{ex} = 447 \text{ nm}, [13] = 10 \text{ μM}. \)

Figure S40. Emission response of 14 in presence and absence of 20 μM HSA in 9:1 PBS:MeCN (PH=7.4). \( \lambda_{ex} = 419 \text{ nm}, [14] = 10 \text{ μM}. \)
**Figure S41.** Emission response of 15 in presence and absence of 20 μM HSA in 9:1 PBS:MeCN (PH=7.4). $\lambda_{ex}=450$ nm, $[15]=10$ μM.

**Figure S42.** Emission response of 16 in presence and absence of different amino acids in 9:1 PBS:MeCN (PH=7.4). $\lambda_{ex}=396$ nm, $[16]=10$ μM.
**Figure S43.** Saturation binding assay generated by GraphPad Prism using various concentrations of 16 (0-100 μM) towards HSA (20 μM).

**Figure S44.** Emission response of 16.HSA complex in presence and absence of SDS (20 μM) in 9:1 PBS:MeCN (pH= 7.4). λ<sub>ex</sub> = 396 nm, [16] = 10 μM, [HSA] = 20 μM.
Table S1. Photophysical properties of 6-16.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>λ&lt;sub&gt;ex&lt;/sub&gt; in MeCN (nm)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; in MeCN (nm)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; in MeCN:PBS (1:9) (nm)</th>
<th>Stokes shift (MeCN)</th>
<th>Φ (%) in aerated MeCN&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Φ (%) in degassed MeCN&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Φ (%) in MeCN:PBS (1:9)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>326</td>
<td>385</td>
<td>nd&lt;sup&gt;b&lt;/sup&gt;</td>
<td>59</td>
<td>nd</td>
<td>3.2</td>
<td>nd</td>
</tr>
<tr>
<td>7</td>
<td>340</td>
<td>444</td>
<td>nd</td>
<td>104</td>
<td>nd</td>
<td>2.1</td>
<td>nd</td>
</tr>
<tr>
<td>8</td>
<td>337</td>
<td>410</td>
<td>nd</td>
<td>73</td>
<td>nd</td>
<td>3.7</td>
<td>nd</td>
</tr>
<tr>
<td>9</td>
<td>341</td>
<td>420</td>
<td>423</td>
<td>79</td>
<td>0.7</td>
<td>4.1</td>
<td>1.1</td>
</tr>
<tr>
<td>10</td>
<td>394</td>
<td>526</td>
<td>529</td>
<td>132</td>
<td>1.4</td>
<td>6.3</td>
<td>1.4</td>
</tr>
<tr>
<td>11</td>
<td>334</td>
<td>474</td>
<td>476</td>
<td>140</td>
<td>3.1</td>
<td>8.1</td>
<td>11.5</td>
</tr>
<tr>
<td>12</td>
<td>364</td>
<td>469</td>
<td>518</td>
<td>105</td>
<td>5.1</td>
<td>9.4</td>
<td>10.1</td>
</tr>
<tr>
<td>13</td>
<td>447</td>
<td>547</td>
<td>563</td>
<td>100</td>
<td>6.2</td>
<td>12.1</td>
<td>1.6</td>
</tr>
<tr>
<td>14</td>
<td>419</td>
<td>543</td>
<td>549</td>
<td>124</td>
<td>6.8</td>
<td>17.4</td>
<td>19.8</td>
</tr>
<tr>
<td>15</td>
<td>450</td>
<td>527</td>
<td>521</td>
<td>77</td>
<td>8.4</td>
<td>14.5</td>
<td>1.4</td>
</tr>
<tr>
<td>16</td>
<td>396</td>
<td>505</td>
<td>595</td>
<td>109</td>
<td>3.8</td>
<td>10.3</td>
<td>10.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> Quantum yields calculated using tris(2,2'-bipyridyl)ruthenium(II) chloride in aerated water (Φ = 2.8 %)<sup>1</sup> as a reference.

<sup>b</sup>nd: not determined.
Table 2. Crystallographic data for 12.

<table>
<thead>
<tr>
<th></th>
<th>Formula</th>
<th>C$<em>{31}$H$</em>{18}$ClN$_2$O$_3$ReS$_2$C$_7$H$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td></td>
<td>C$<em>{31}$H$</em>{18}$ClN$_2$O$_3$ReS$_2$C$_7$H$_8$</td>
</tr>
<tr>
<td><strong>FW</strong></td>
<td></td>
<td>844.38</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td></td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td></td>
<td>P - 1</td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td></td>
<td>8.7755(9)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td></td>
<td>13.4717(14)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td></td>
<td>15.1412(15)</td>
</tr>
<tr>
<td><strong>α/°</strong></td>
<td></td>
<td>78.884(5)</td>
</tr>
<tr>
<td><strong>β/°</strong></td>
<td></td>
<td>77.789(5)</td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
<td></td>
<td>72.824(5)</td>
</tr>
<tr>
<td><strong>V/Å$^3$</strong></td>
<td></td>
<td>1655.11(16)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td><strong>D$_{calc}$</strong></td>
<td></td>
<td>1.694</td>
</tr>
<tr>
<td><strong>μ (mm$^{-1}$)</strong></td>
<td></td>
<td>3.919</td>
</tr>
<tr>
<td><strong>T/K</strong></td>
<td></td>
<td>190.15</td>
</tr>
<tr>
<td><strong>No. of reflections</strong></td>
<td></td>
<td>30896</td>
</tr>
<tr>
<td><strong>No. of unique reflections</strong></td>
<td></td>
<td>9988</td>
</tr>
<tr>
<td><strong>No. of reflections with l &gt; 2σ(l)</strong></td>
<td></td>
<td>7097</td>
</tr>
<tr>
<td><strong>R$_1$ [l &gt; 2σ(l)]</strong></td>
<td></td>
<td>0.0185</td>
</tr>
<tr>
<td><strong>wR$_2$</strong></td>
<td></td>
<td>0.0408</td>
</tr>
<tr>
<td><strong>CCDC No.</strong></td>
<td></td>
<td>1571905</td>
</tr>
</tbody>
</table>

This complex crystallized with a full molecule in the asymmetric unit along with one full disordered toluene solvate molecule. One thiophene ring is disordered by a two-fold rotation about the C5-C11 bond. The C5-C11 and C5-C11' bonds were restrained to be the same. The anisotropic displacement parameters (adp's) of the disordered pair were restrained by the rigid bond and similarity restraints. The toluene molecule was disordered over an inversion center with two positions that are coplanar and in a 180° angle relative to each other. Toluene solvate was refined by using geometry restraints with two positions for each atom.
**Figure S45.** ORTEP plot of 12-toluene.

**References:**