

**Photoinduced processes in rhenium(I) terpyridine complexes bearing remote amine groups. New insights from transient absorption spectroscopy**

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## X-Ray analysis

**Table S1.** Crystal data and structure refinement for **1**.

|                                                              | <b>1</b>                                                           |
|--------------------------------------------------------------|--------------------------------------------------------------------|
| Empirical formula                                            | C <sub>29</sub> H <sub>25</sub> ClN <sub>5</sub> O <sub>3</sub> Re |
| Formula weight                                               | 713.19                                                             |
| <i>T</i> , K                                                 | 295.0(2)                                                           |
| Wavelength, Å                                                | 0.71073                                                            |
| Crystal system                                               | Monoclinic                                                         |
| Space group                                                  | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                 |
| Unit cell dimensions, Å and °                                |                                                                    |
| <i>a</i>                                                     | 15.2721(6)                                                         |
| <i>b</i>                                                     | 11.5579(6)                                                         |
| <i>c</i>                                                     | 32.1005(16)                                                        |
| $\beta$                                                      | 102.434(5)                                                         |
| <i>V</i> , Å <sup>3</sup>                                    | 5533.3(5)                                                          |
| <i>Z</i>                                                     | 8                                                                  |
| <i>D<sub>c</sub></i> , g cm <sup>-3</sup>                    | 1.712                                                              |
| Absorption coefficient, mm <sup>-1</sup>                     | 4.529                                                              |
| <i>F</i> (000)                                               | 2800.0                                                             |
| Crystal size, mm                                             | 0.26×0.13×0.03                                                     |
| $\theta$ range for data collection, °                        | 3.43 to 29.47                                                      |
| Index ranges                                                 | -18 ≤ <i>h</i> ≤ 18<br>-13 ≤ <i>k</i> ≤ 10<br>-38 ≤ <i>l</i> ≤ 33  |
| Reflections collected                                        | 24779                                                              |
| Independent reflections                                      | 9760 [ <i>R</i> <sub>int</sub> = 0.0396]                           |
| Completeness to 2 $\theta$                                   | 99.7                                                               |
| Min. and max. transm.                                        | 0.170 and 1.000                                                    |
| Data / restraints / parameters                               | 9760/0/705                                                         |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                     | 0.982                                                              |
| Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] |                                                                    |
| <i>R</i> <sub>1</sub>                                        | 0.0337                                                             |
| <i>wR</i> <sub>2</sub>                                       | 0.0643                                                             |
| <i>R</i> indices (all data)                                  |                                                                    |
| <i>R</i> <sub>1</sub>                                        | 0.0518                                                             |
| <i>wR</i> <sub>2</sub>                                       | 0.0698                                                             |
| Largest diff. peak and hole, e Å <sup>-3</sup>               | 0.83 and -0.61                                                     |
| CCDC number                                                  | 2205501                                                            |

**Table S2.** Bond lengths [Å] and angles [°] for **1**.

| Bond lengths [Å] |            | Bond angles [°]  |            |
|------------------|------------|------------------|------------|
| Re(1)–C(1)       | 1.893(6)   | C(2)–Re(1)–C(1)  | 89.7(2)    |
| Re(1)–C(2)       | 1.926(6)   | C(3)–Re(1)–C(1)  | 86.0(2)    |
| Re(1)–C(3)       | 1.927(6)   | C(3)–Re(1)–C(2)  | 91.0(2)    |
| Re(1)–N(1)       | 2.205(4)   | C(1)–Re(1)–N(1)  | 168.86(16) |
| Re(1)–N(2)       | 2.171(4)   | C(2)–Re(1)–N(1)  | 92.7(2)    |
| Re(1)–Cl(1)      | 2.4889(13) | C(3)–Re(1)–N(1)  | 102.38(19) |
| Re(2)–C(30)      | 1.870(7)   | C(1)–Re(1)–N(2)  | 96.94(19)  |
| Re(2)–C(31)      | 1.902(6)   | C(2)–Re(1)–N(2)  | 92.7(2)    |
| Re(2)–C(32)      | 1.926(6)   | C(3)–Re(1)–N(2)  | 175.30(19) |
| Re(2)–N(6)       | 2.199(4)   | N(1)–Re(1)–N(2)  | 74.26(14)  |
| Re(2)–N(7)       | 2.171(4)   | C(1)–Re(1)–Cl(1) | 91.57(18)  |
| Re(2)–Cl(2)      | 2.4981(13) | C(2)–Re(1)–Cl(1) | 177.71(18) |
| C(1)–O(1)        | 1.158(6)   | C(3)–Re(1)–Cl(1) | 90.94(17)  |
| C(2)–O(2)        | 1.105(7)   | N(1)–Re(1)–Cl(1) | 81.05(10)  |

|            |          |                   |            |
|------------|----------|-------------------|------------|
| C(3)–O(3)  | 1.146(6) | N(2)–Re(1)–Cl(1)  | 85.31(10)  |
| C(30)–O(4) | 1.167(7) | C(30)–Re(2)–C(31) | 88.8(3)    |
| C(31)–O(5) | 1.143(6) | C(30)–Re(2)–C(32) | 85.7(2)    |
| C(32)–O(6) | 1.140(6) | C(31)–Re(2)–C(32) | 87.2(2)    |
|            |          | C(30)–Re(2)–N(6)  | 169.82(17) |
|            |          | C(30)–Re(2)–N(7)  | 97.3(2)    |
|            |          | C(31)–Re(2)–N(6)  | 97.03(19)  |
|            |          | C(31)–Re(2)–N(7)  | 95.93(19)  |
|            |          | C(32)–Re(2)–N(6)  | 102.88(18) |
|            |          | C(32)–Re(2)–N(7)  | 175.68(18) |
|            |          | N(6)–Re(2)–N(7)   | 73.82(14)  |
|            |          | N(6)–Re(2)–Cl(2)  | 81.54(10)  |
|            |          | N(7)–Re(2)–Cl(2)  | 83.77(10)  |
|            |          | C(30)–Re(2)–Cl(2) | 92.6(2)    |
|            |          | C(31)–Re(2)–Cl(2) | 178.57(17) |
|            |          | C(32)–Re(2)–Cl(2) | 93.03(19)  |

Table S3. Short intramolecular contacts detected in the structure of **1**.

| D—H...A                          | D—H  | H...A | D...A<br>[Å] | D—H...A<br>[°] |
|----------------------------------|------|-------|--------------|----------------|
| 1                                |      |       |              |                |
| C(15)–H(15)...Cl(2) <sup>a</sup> | 0.93 | 2.80  | 3.717(5)     | 169.00         |
| C(20)–H(20)...Cl(2) <sup>a</sup> | 0.93 | 2.81  | 3.558(5)     | 138.00         |
| C(49)–H(49)...Cl(1) <sup>b</sup> | 0.93 | 2.81  | 3.663(5)     | 153.00         |

Symmetry transformations used to generate equivalent atoms: (a) = 1+x, y, z; (b) = –1+x, y, z.

Table S4. Short  $\pi$ ... $\pi$  interactions for **1**.

| Cg(I)...Cg(J)              | Cg(I)...Cg(J) [Å] | $\alpha$ [°] | $\beta$ [°] | $\gamma$ [°] | Cg(I)-Perp [Å] | Cg(J)-Perp [Å] |
|----------------------------|-------------------|--------------|-------------|--------------|----------------|----------------|
| 1                          |                   |              |             |              |                |                |
| Cg(1)...Cg(2) <sup>a</sup> | 3.977(3)          | 5.7(2)       | 33.99       | 29.71        | –3.454(2)      | 3.297(2)       |

$\alpha$  = dihedral angle between Cg(I) and Cg(J); Cg(I)-Perp = Perpendicular distance of Cg(I) on ring J; Cg(J)-Perp = perpendicular distance of Cg(J) on ring I;  $\beta$  = angle Cg(I)→Cg(J) vector and normal to ring I;  $\gamma$  = angle Cg(I) →Cg(J) vector and normal to plane J;

Cg(1) = N(2)/C(14)/C(15)/C(16)/C(17)/C(18);

Cg(2) = C(48)/C(49)/C(50)/C(51)/C(52)/C(53);

Symmetry codes: (a) = 1+x, y, z.

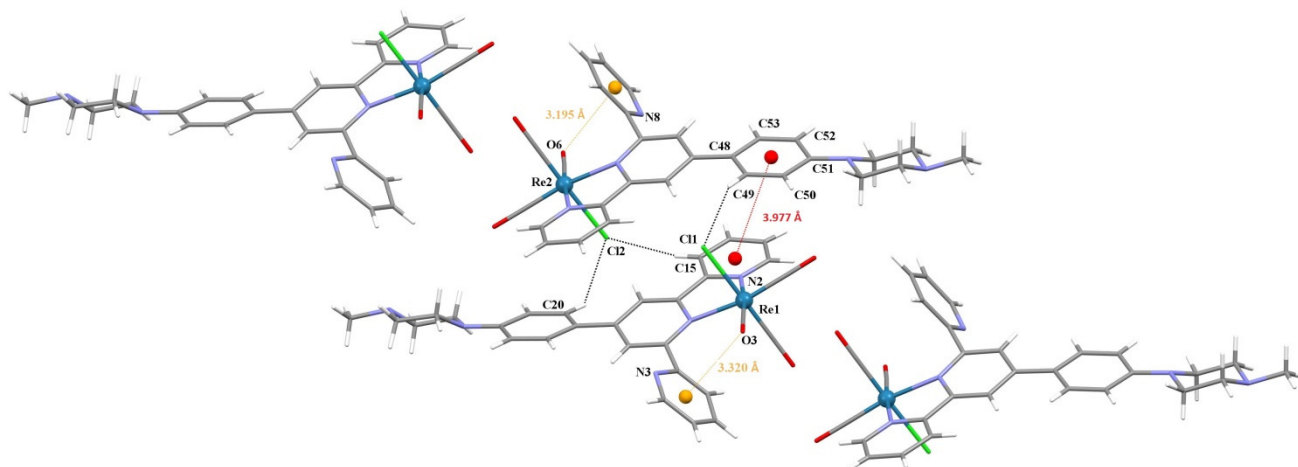
Table S5. C—O...Cg(J) ( $\pi$ -ring) interactions of **1**.

| Y(I)–X(I)...Cg(J)  | Y(I)–H(I)...Cg(J) [Å] | X(I)-Perp [Å] | $\gamma$ [°] | Y(I)–X(I)...Cg(J) [°] |
|--------------------|-----------------------|---------------|--------------|-----------------------|
| 1                  |                       |               |              |                       |
| C(3)–O(3)...Cg(3)  | 3.320(5)              | 3.289         | 7.88         | 85.6(4)               |
| C(32)–O(6)...Cg(4) | 3.195(5)              | –3.131        | 11.45        | 84.9(4)               |

$\gamma$  = angle X(I)→Cg(J) vector and normal to plane J.

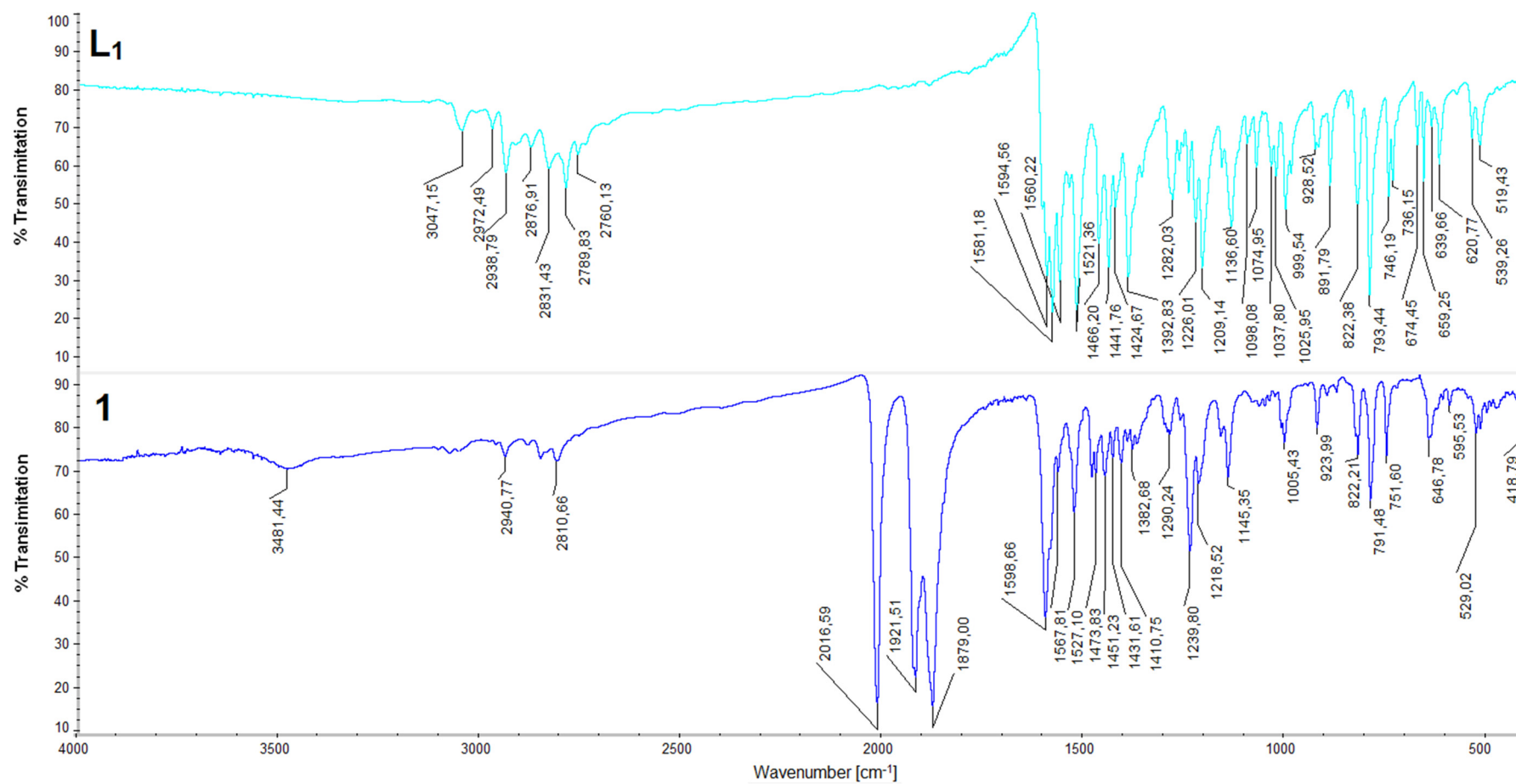
Cg(3) = N(8)/C(38)/C(39)/C(40)/C(41)/C(42);

Cg(4) = N(3)/C(9)/C(10)/C(11)/C(12)/C(13).

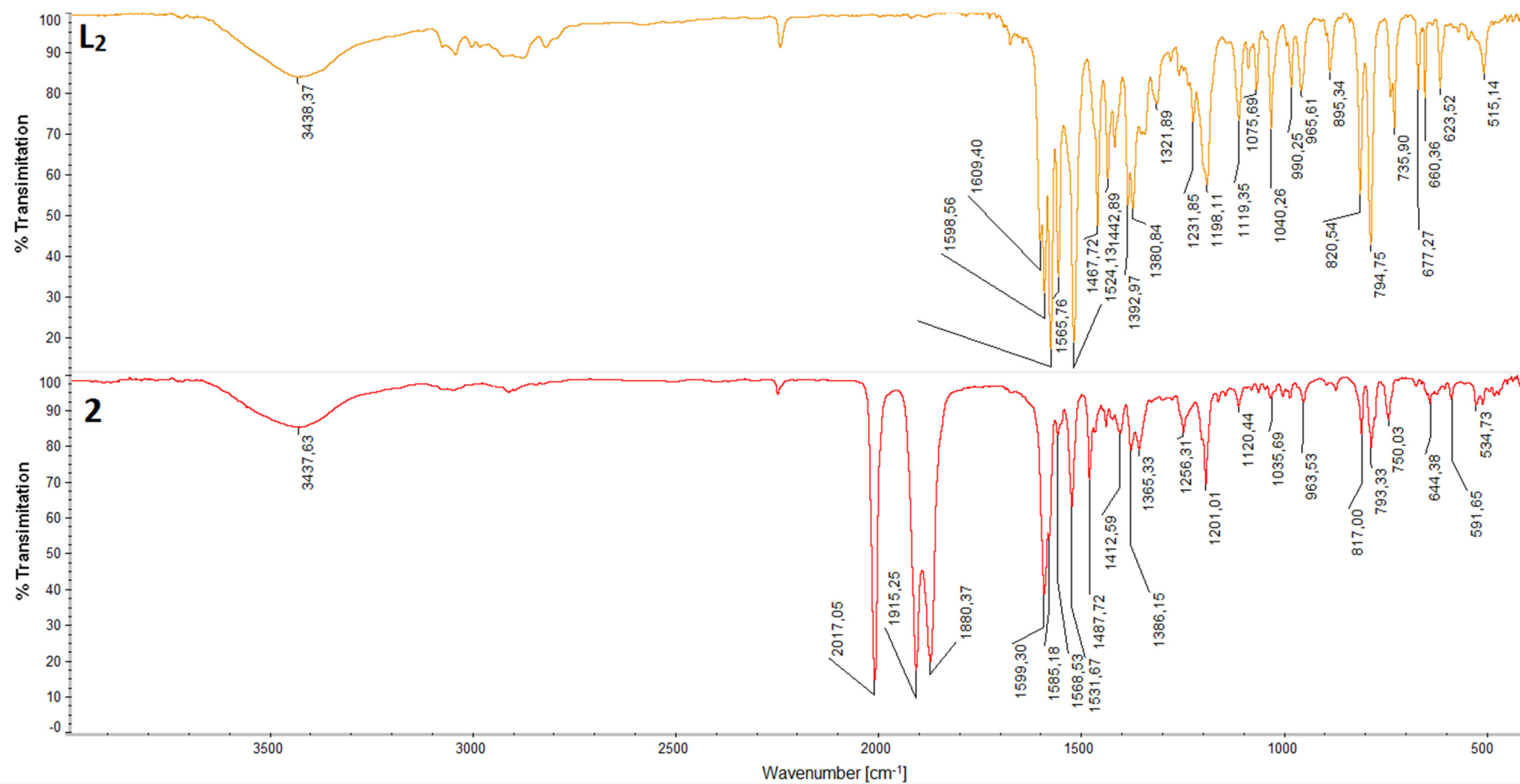


**Figure S1.** View of supramolecular packing of **1** arising from weak  $\pi\cdots\pi$  type and C–O $\cdots\pi$  interactions (red and yellow dashed line) and C–H $\cdots$ Cl short contacts (black dashed line).

## IR spectra

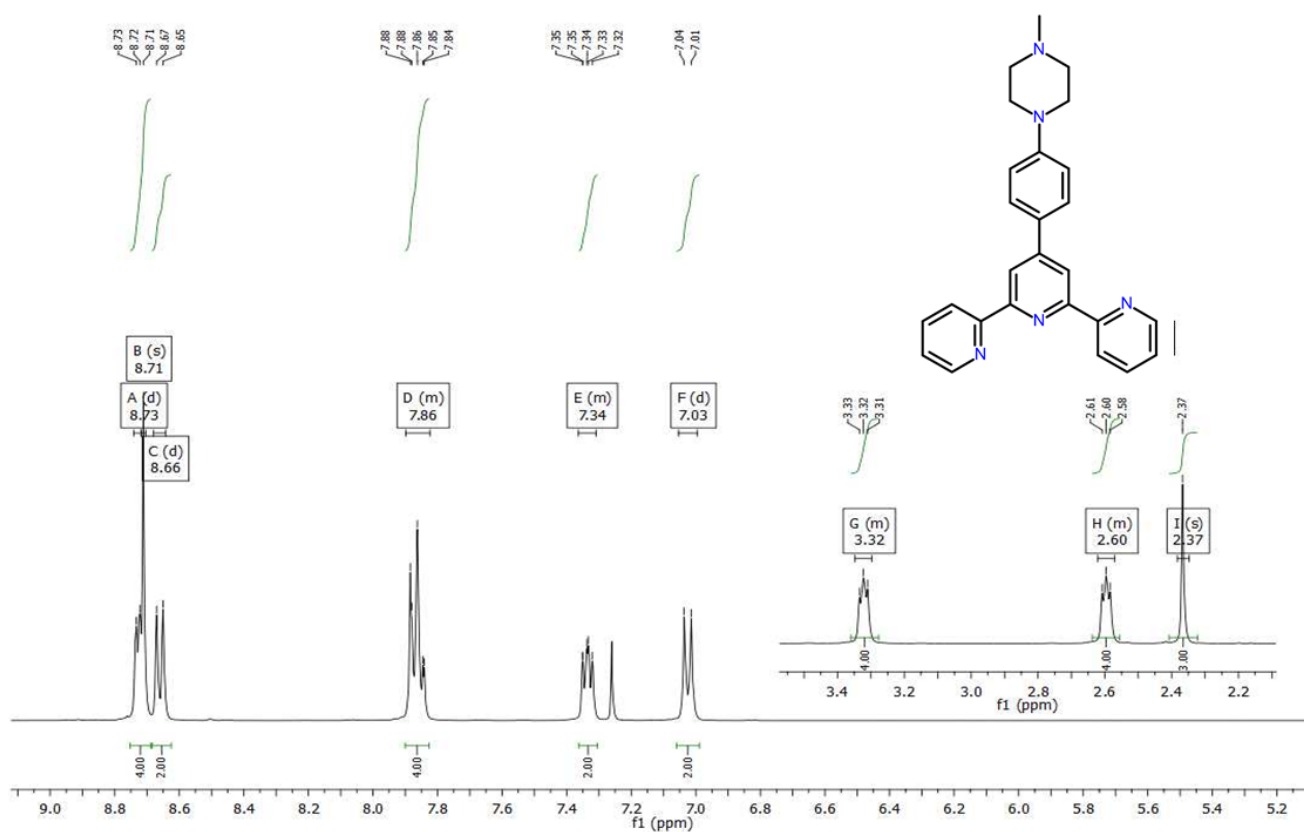


**Figure S2.** FT-IR spectrum of **1** along with FT-IR spectrum of the free ligand.



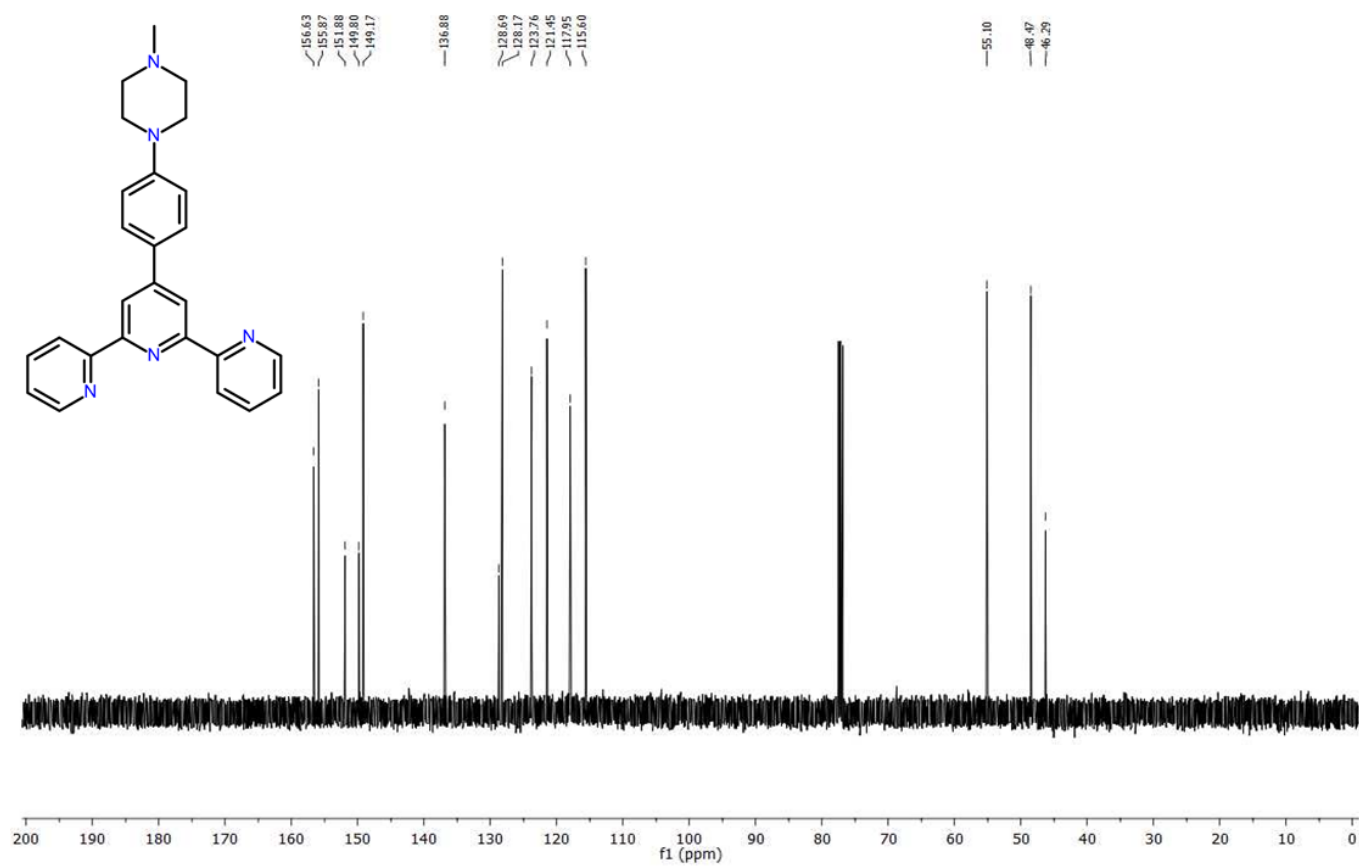
**Figure S3.** FT-IR spectrum of **2** along with FT-IR spectrum of the free ligand.

## NMR spectroscopy



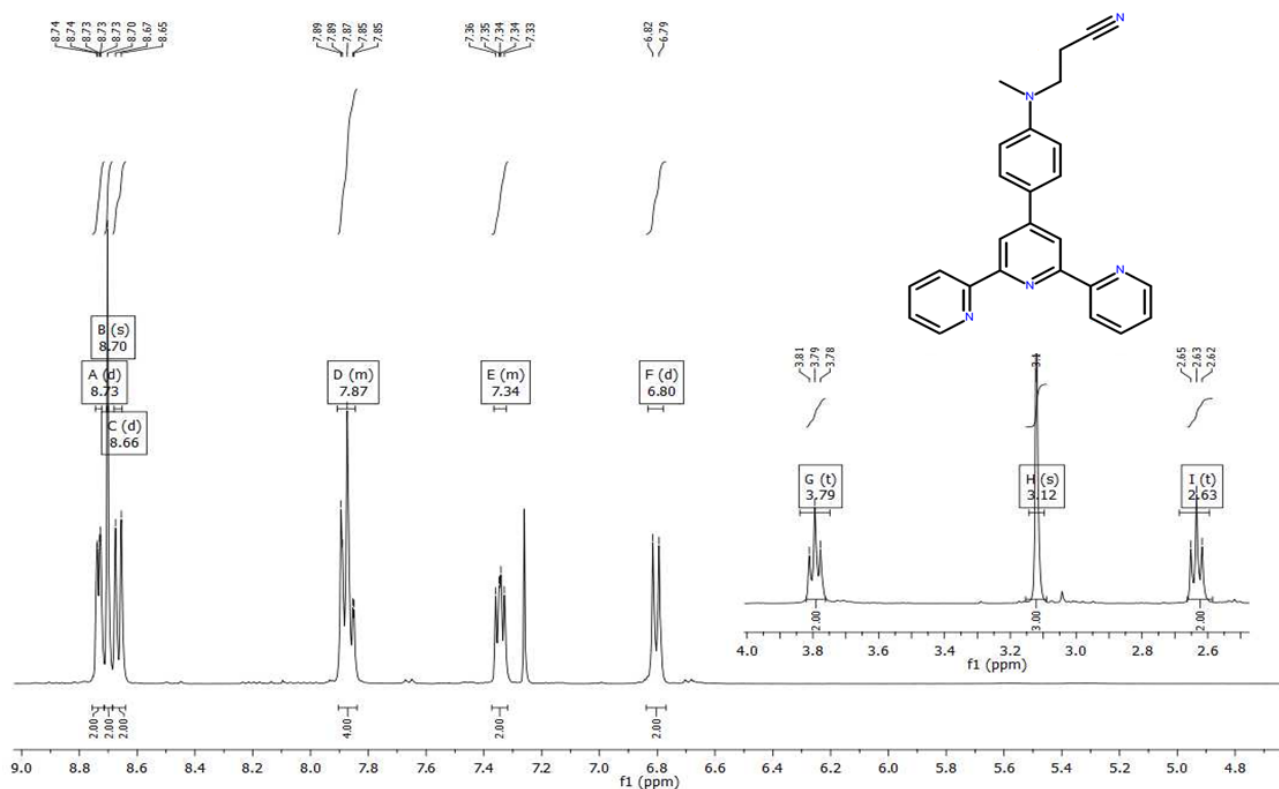
**Figure S4.** <sup>1</sup>H NMR spectrum of **L1**.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.73 (d,  $J$  = 4.8 Hz, 2H), 8.71 (s, 2H), 8.66 (d,  $J$  = 7.9 Hz, 2H), 7.90 – 7.82 (m, 4H), 7.36 – 7.31 (m, 2H), 7.03 (d,  $J$  = 8.8 Hz, 2H), 3.35 – 3.30 (m, 4H), 2.62 – 2.57 (m, 4H), 2.37 (s, 3H).



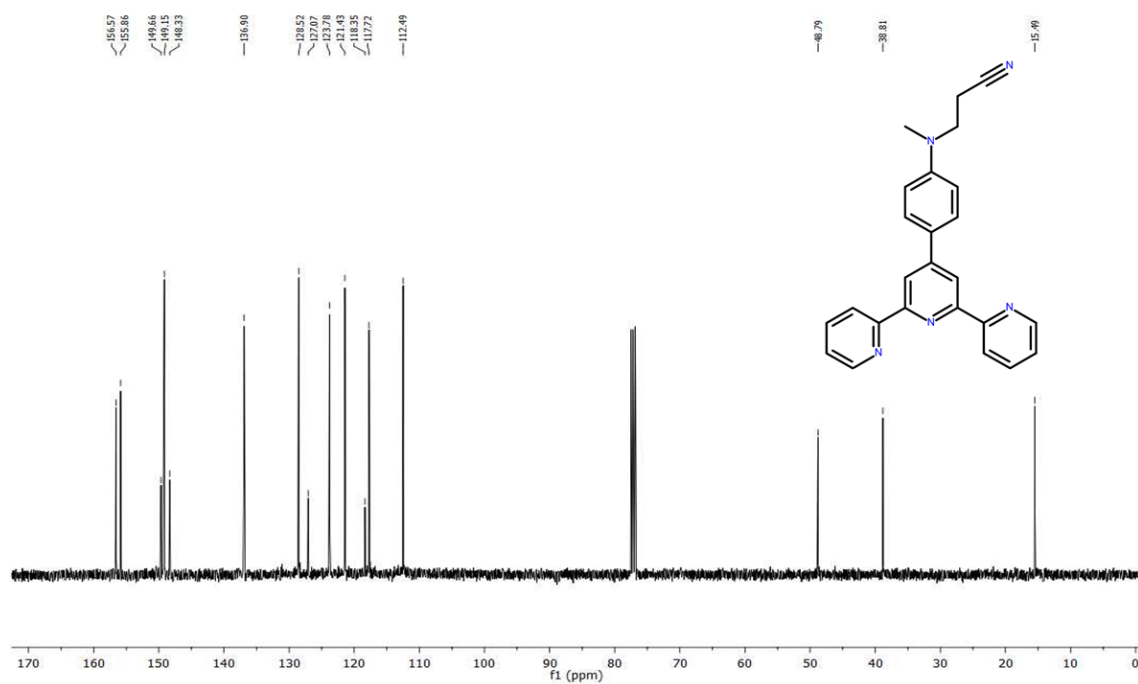
**Figure S5.**  $^{13}\text{C}$  NMR spectrum of L1.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.63, 155.87, 151.88, 149.80, 149.17, 136.88, 128.69, 128.17, 123.76, 121.45, 117.95, 115.60, 55.10, 48.47, 46.29.



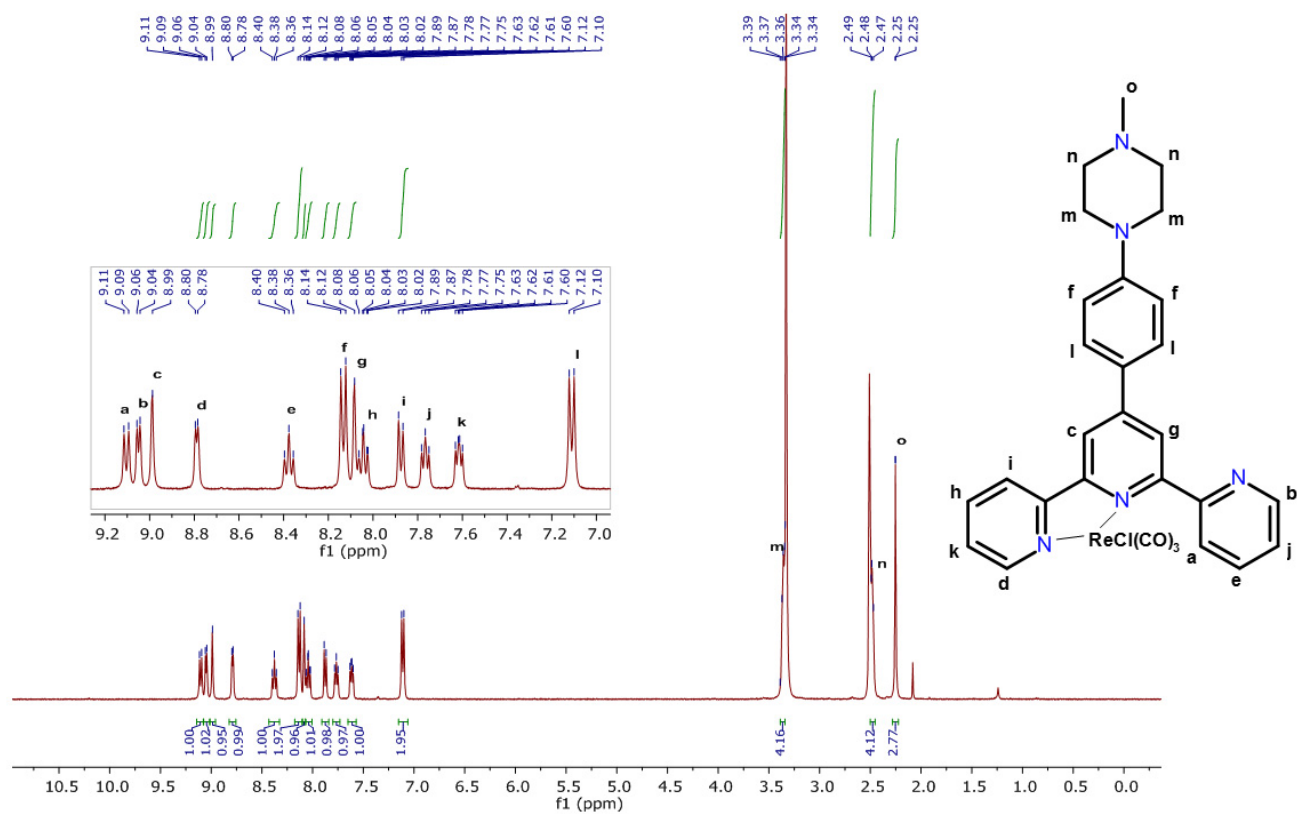
**Figure S6.** <sup>1</sup>H NMR spectrum of L2.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.73 (d,  $J$  = 5.5 Hz, 2H), 8.70 (s, 2H), 8.66 (d,  $J$  = 8.0 Hz, 2H), 7.91 – 7.84 (m, 4H), 7.37 – 7.32 (m, 2H), 6.80 (d,  $J$  = 8.4 Hz, 2H), 3.79 (t,  $J$  = 6.8 Hz, 2H), 3.12 (s, 3H), 2.63 (t,  $J$  = 6.8 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.57, 155.86, 149.66, 149.15, 148.33, 136.90, 128.52, 127.07, 123.78, 121.43, 118.35, 117.72, 112.49, 48.79, 38.81, 15.49.

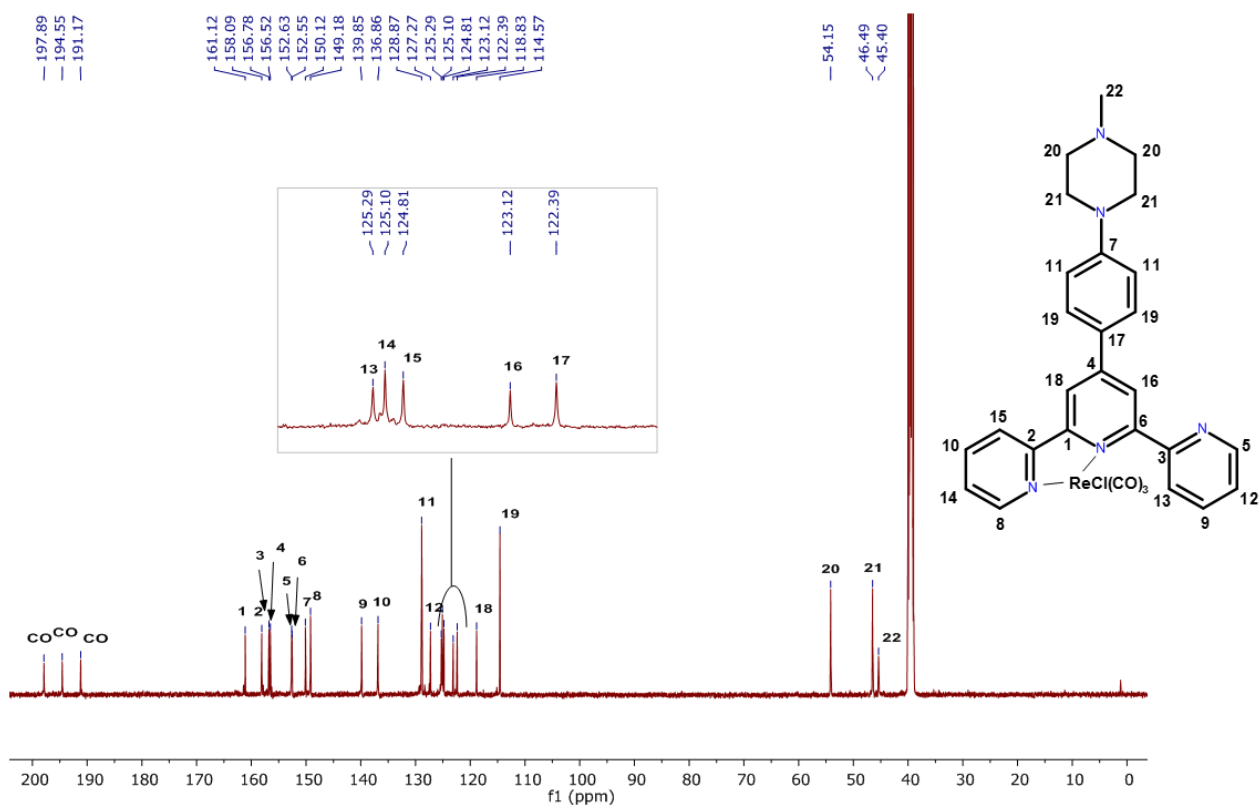


**Figure S7.**  $^{13}\text{C}$  NMR spectrum of L2.

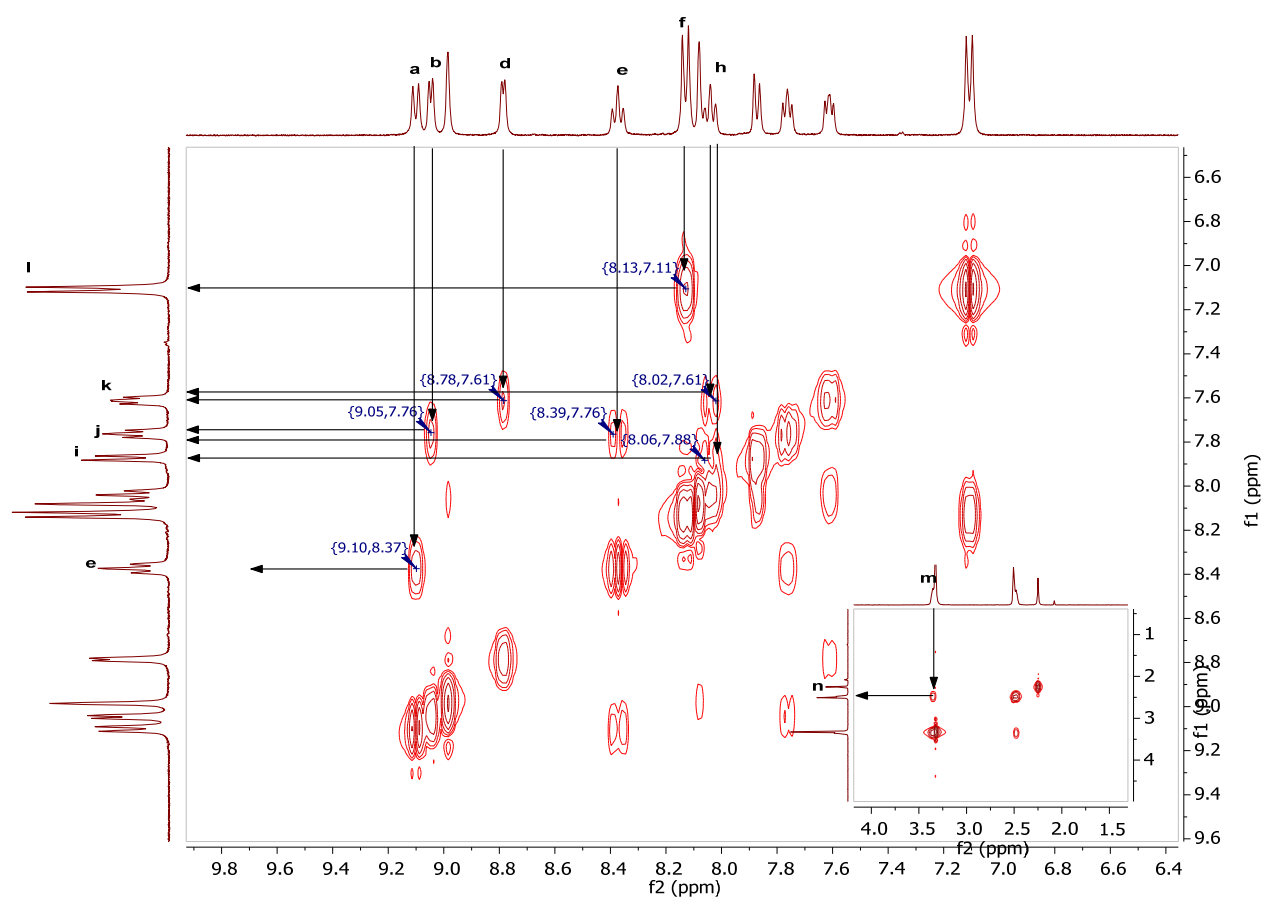
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.57, 155.86, 149.66, 149.15, 148.33, 136.90, 128.52, 127.07, 123.78, 121.43, 118.35, 117.72, 112.49, 48.79, 38.81, 15.49.



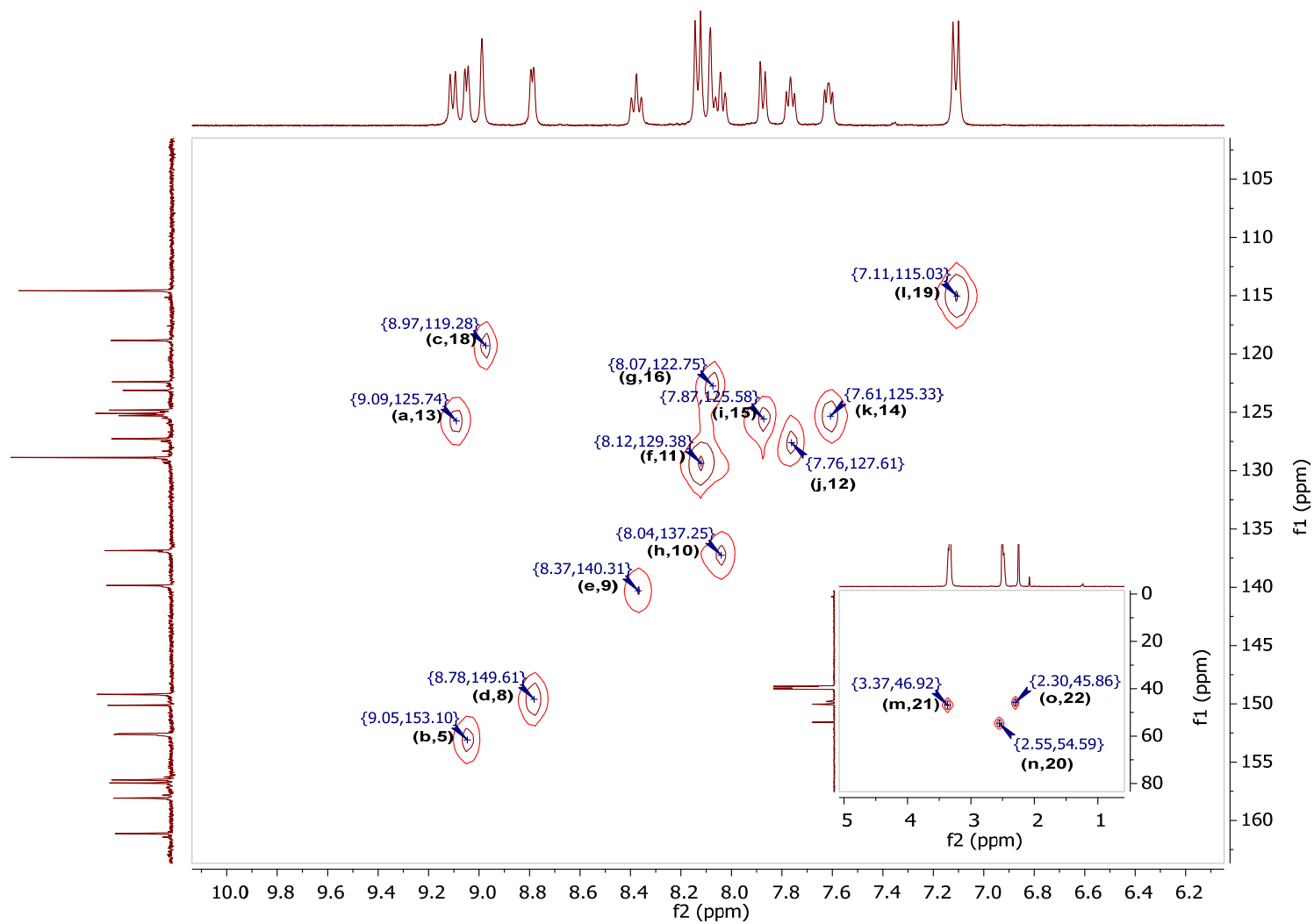
**Figure S8.** <sup>1</sup>H NMR spectrum of **1**.



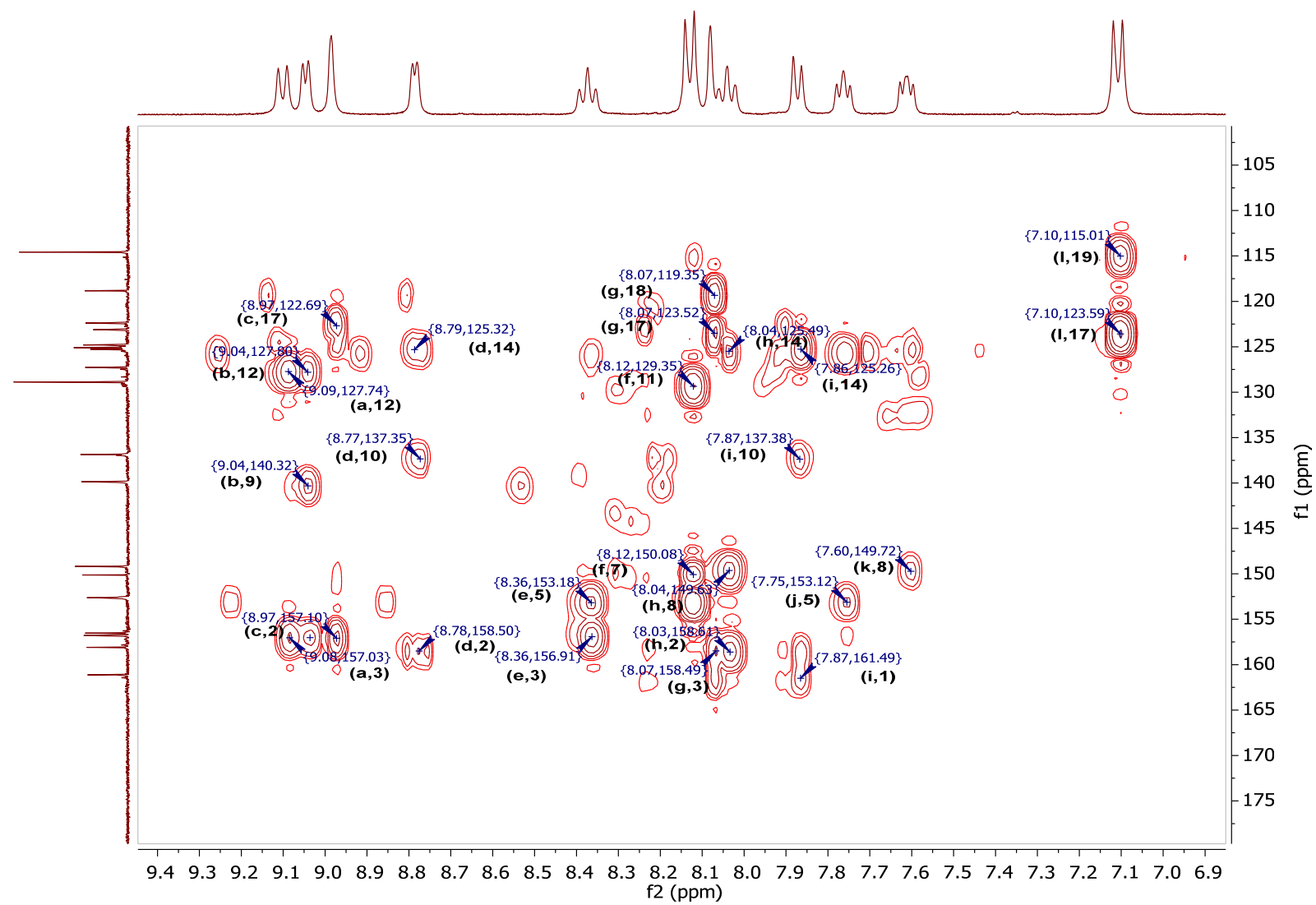
**Figure S9.** <sup>13</sup>C NMR spectrum of **1**.



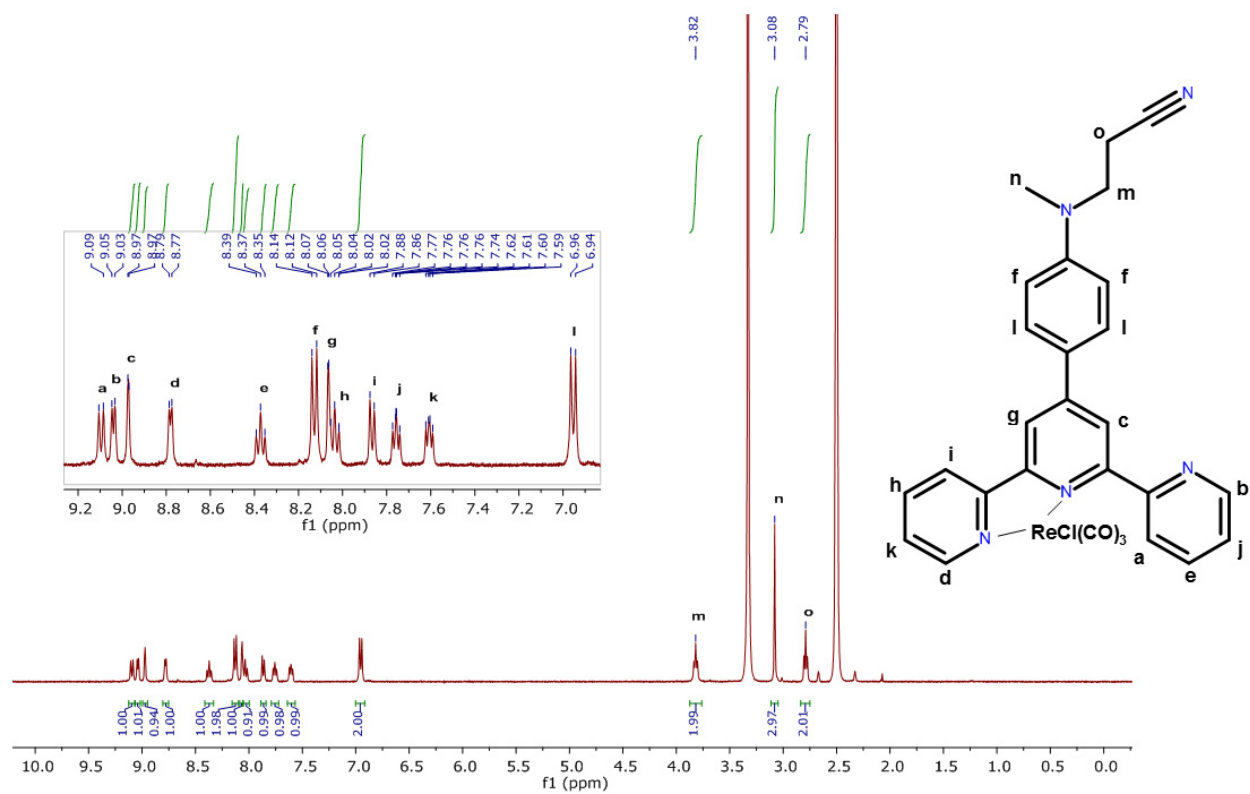
**Figure S10.** <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of **1**.



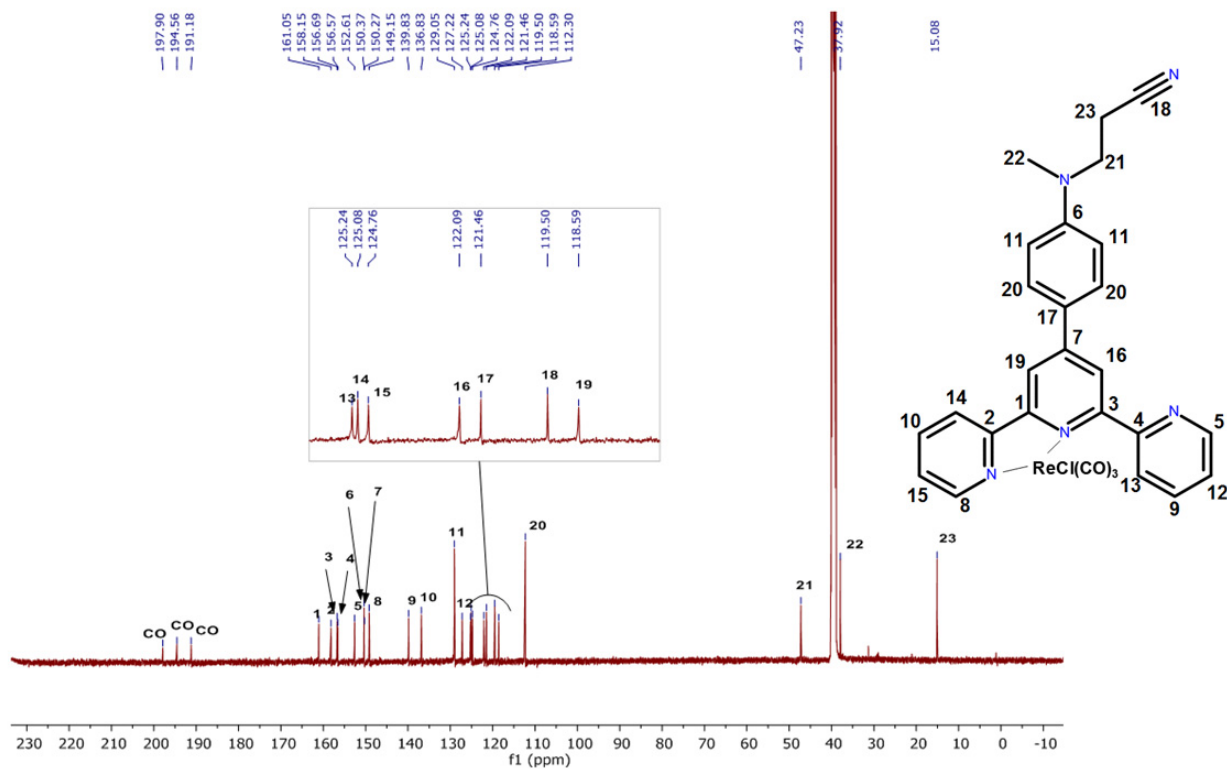
**Figure S11.**  $^1\text{H}$ - $^{13}\text{C}$  HMQC NMR spectrum of **1**.



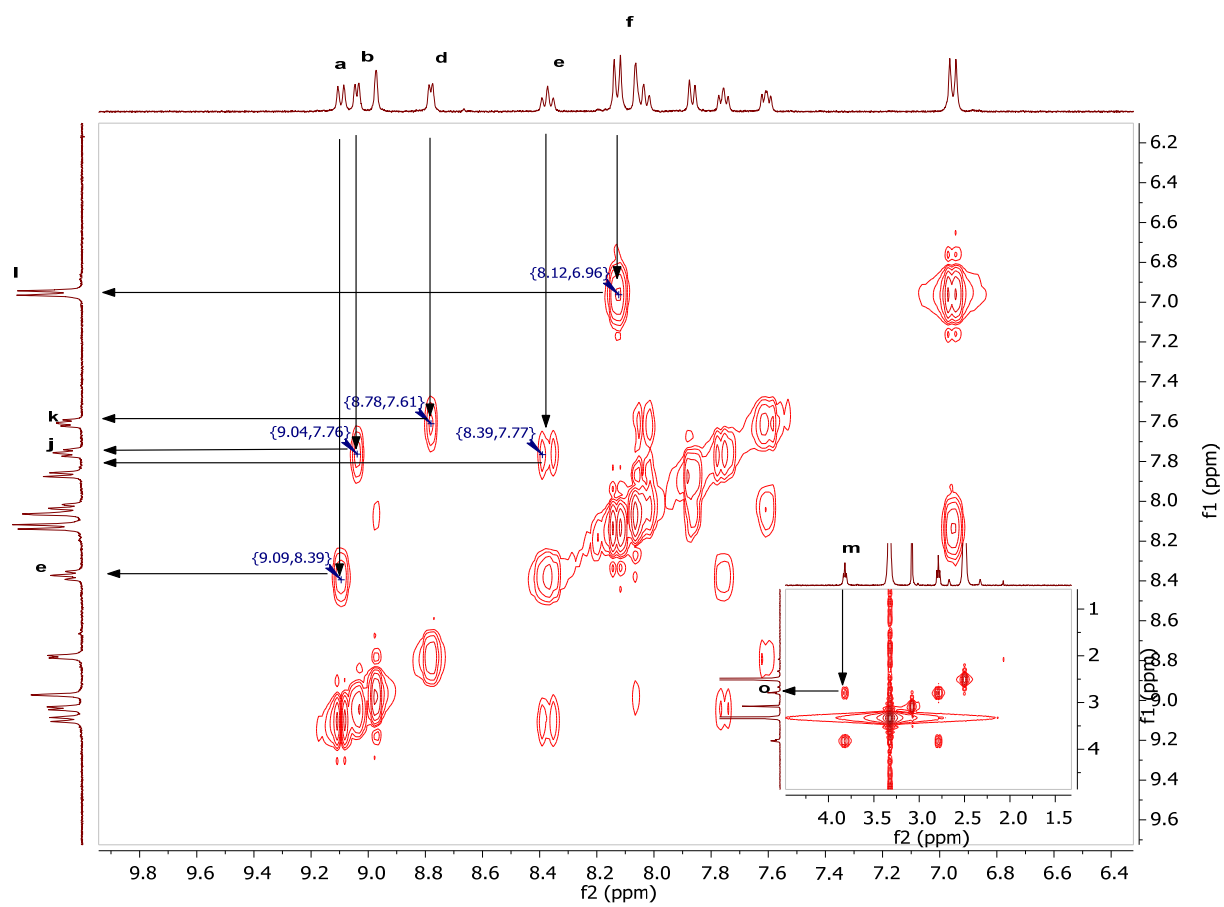
**Figure S12.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of **1**.



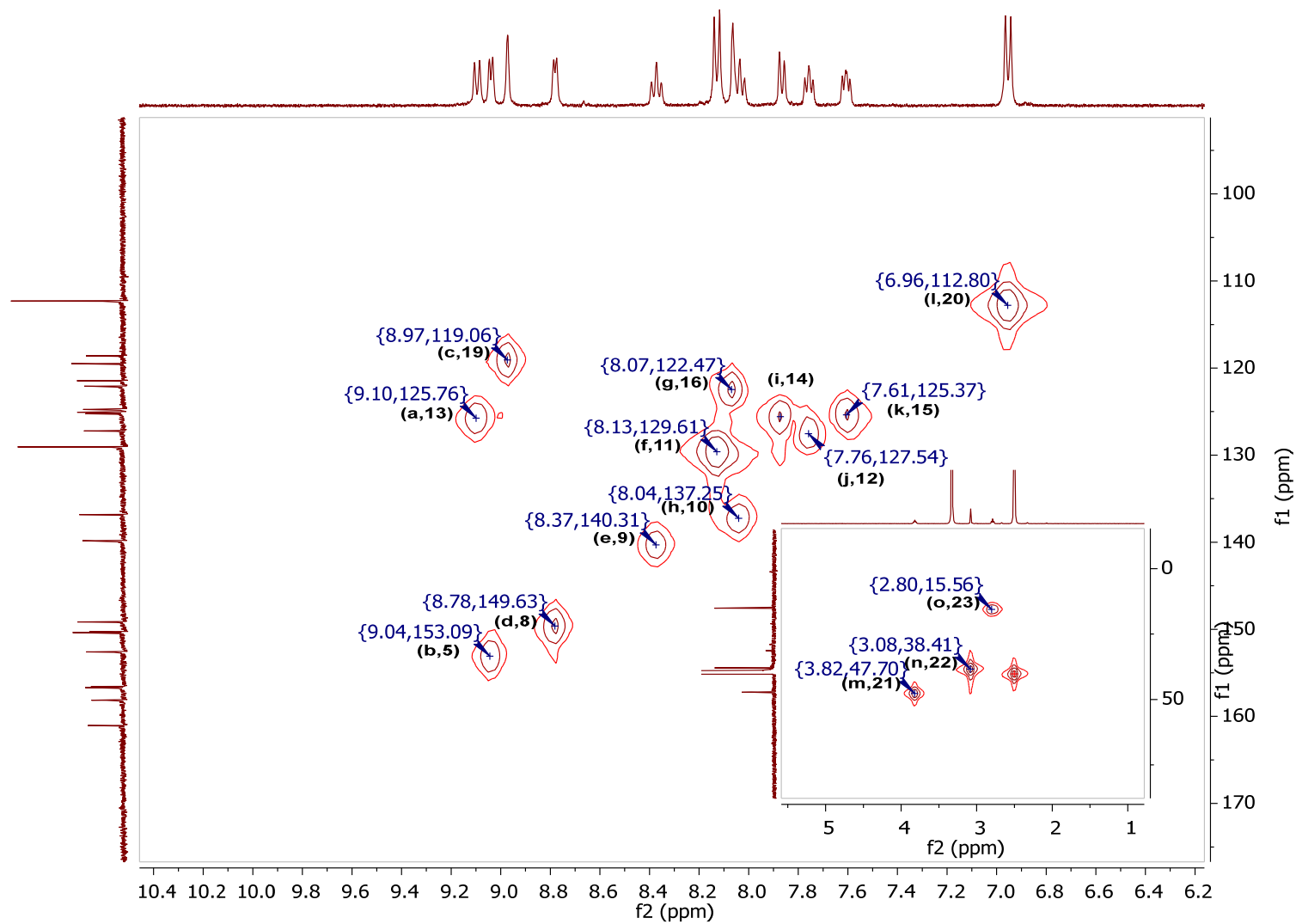
**Figure S13.  $^1\text{H}$  NMR spectrum of 2.**



**Figure S14.  $^{13}\text{C}$  NMR spectrum of 2.**



**Figure S15.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **2**.



**Figure S16.**  $^1\text{H}$ - $^{13}\text{C}$  HMQC NMR spectrum of **2**.

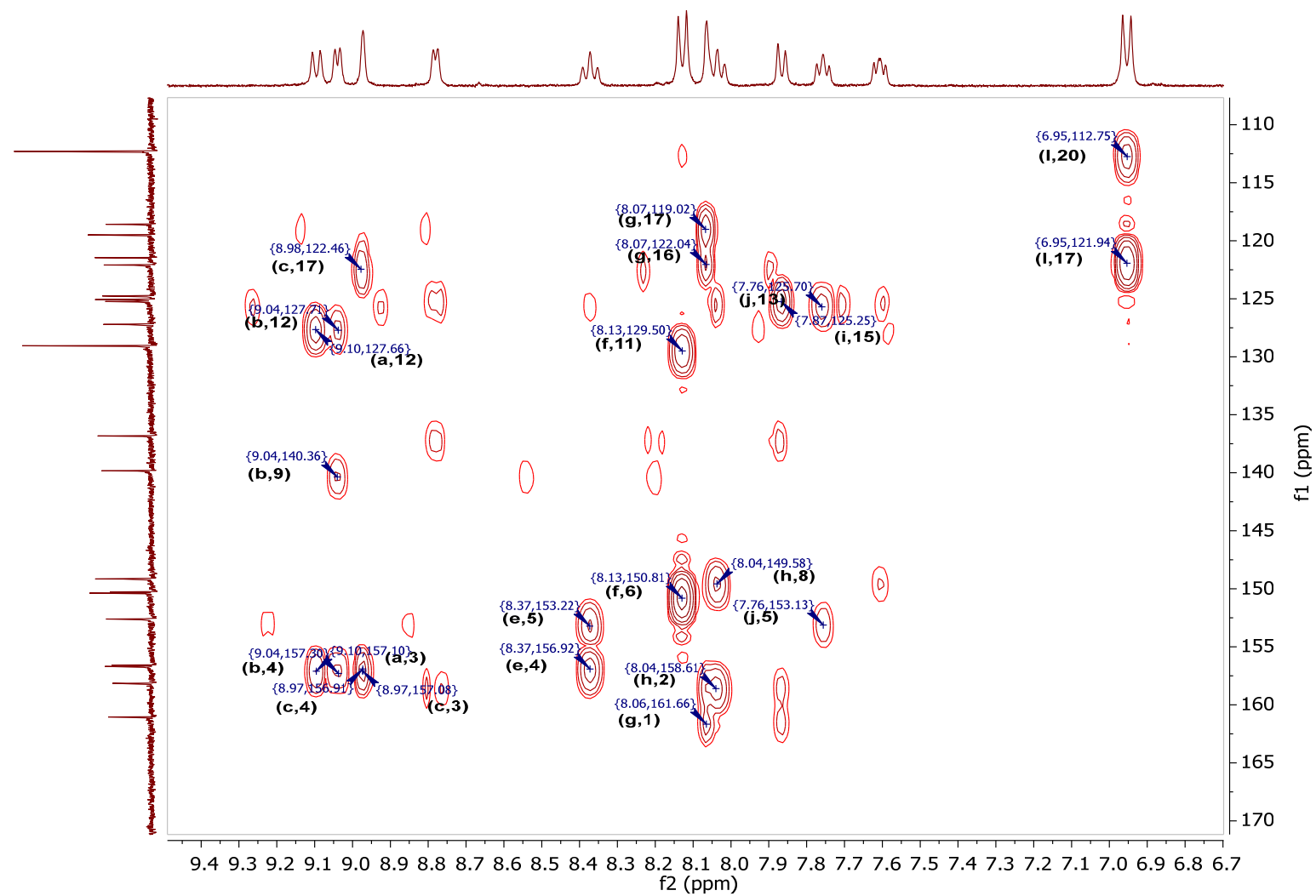


Figure S17.  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of **2**.

## HMRS spectroscopy

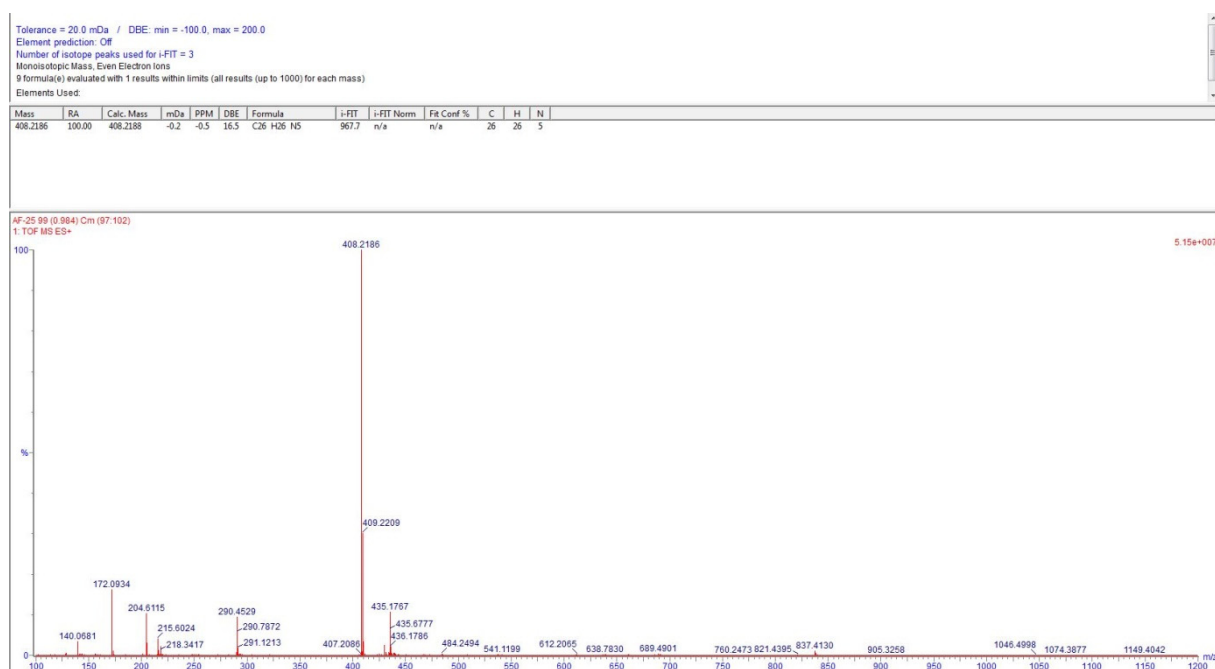


Figure S18. HMRS spectrum of L<sub>1</sub>.

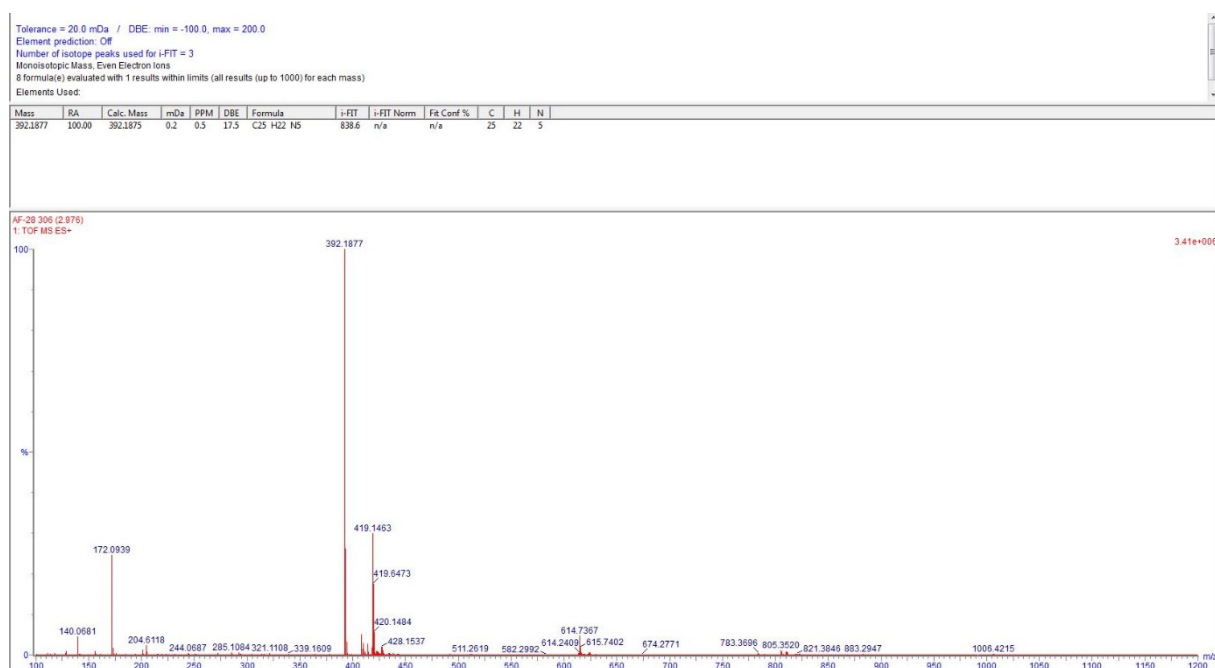


Figure S19. HMRS spectrum of L<sub>2</sub>.

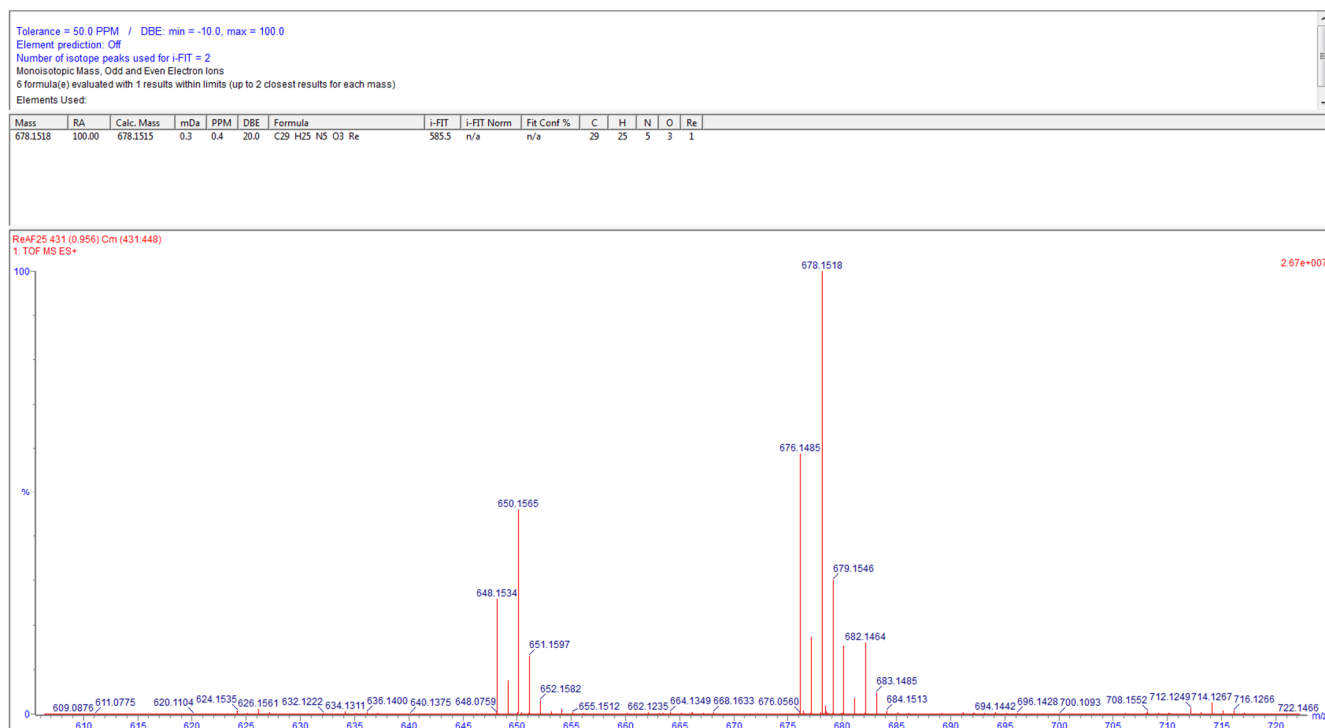


Figure S20. HMRS spectrum of **1**.

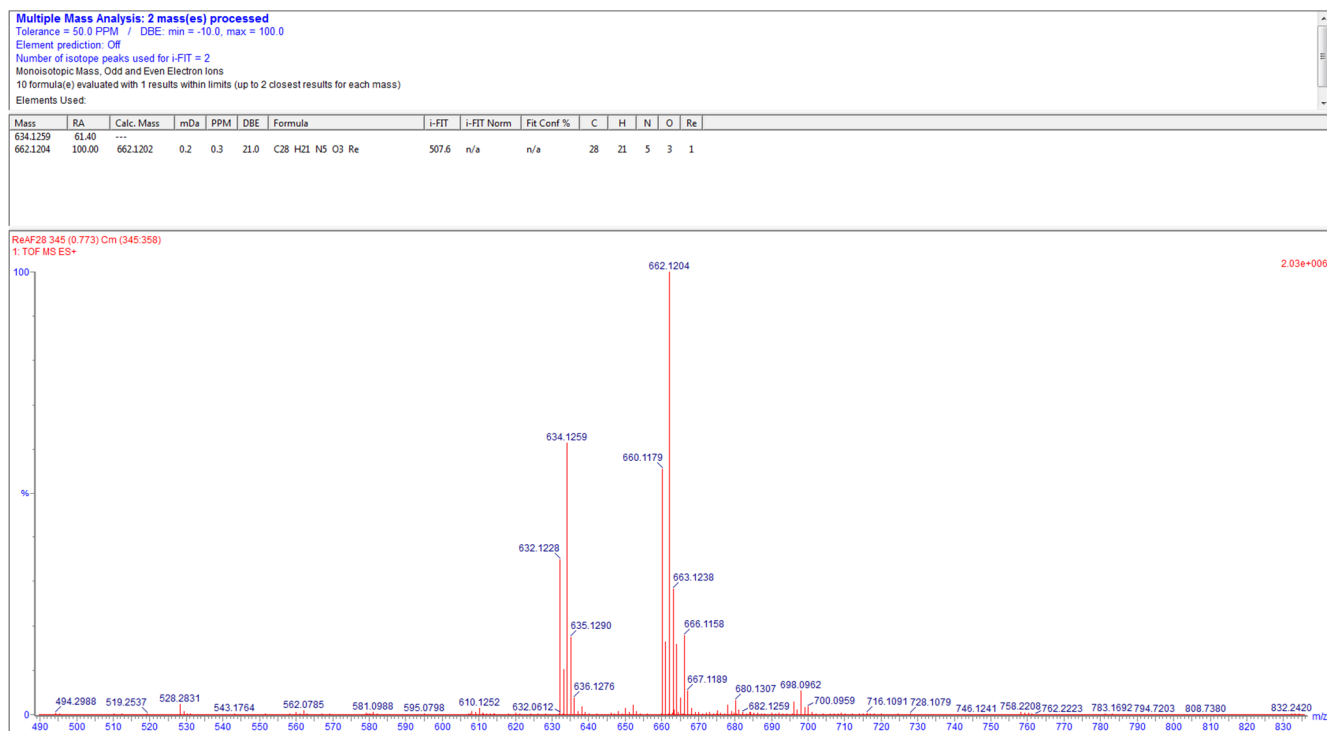
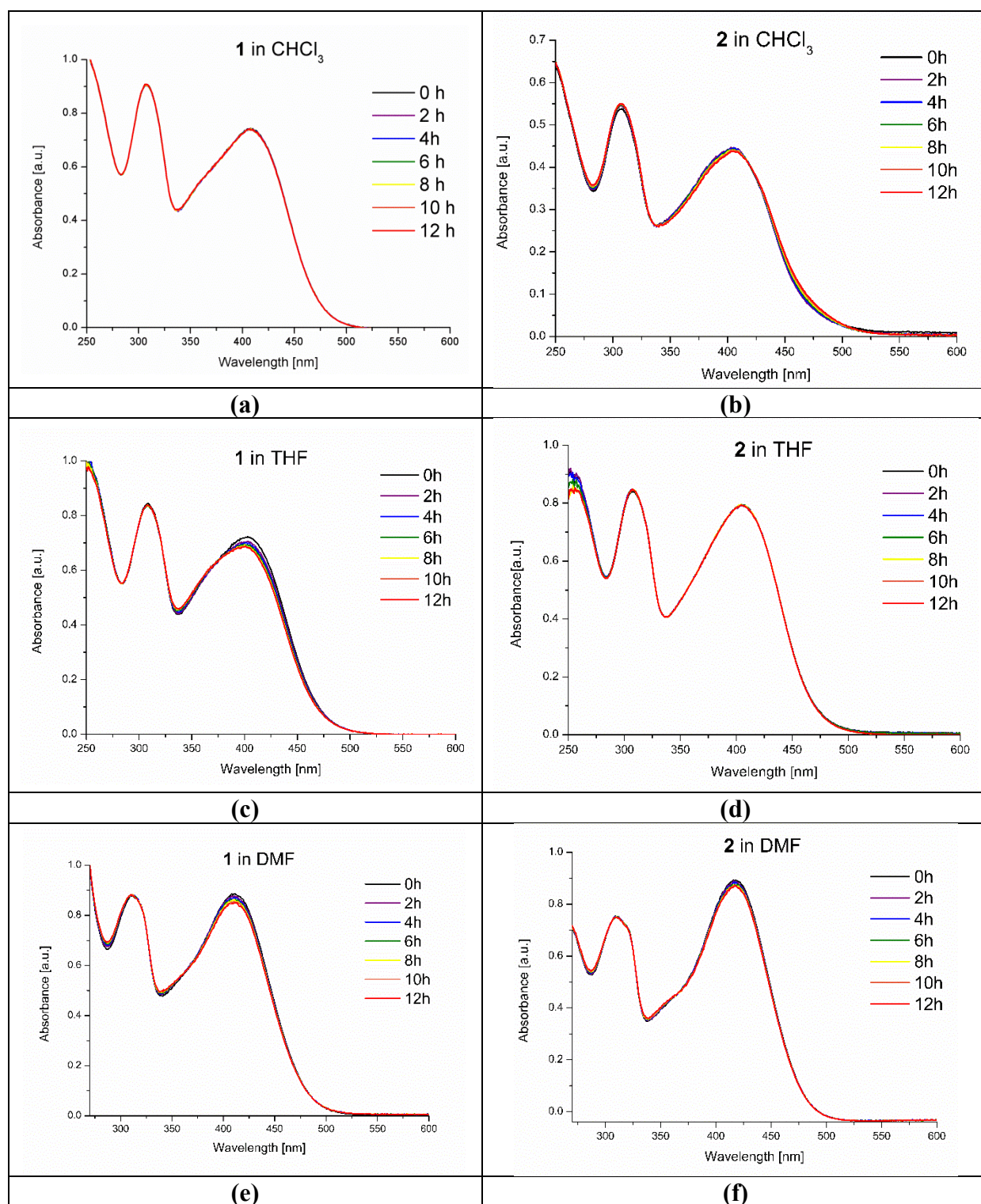
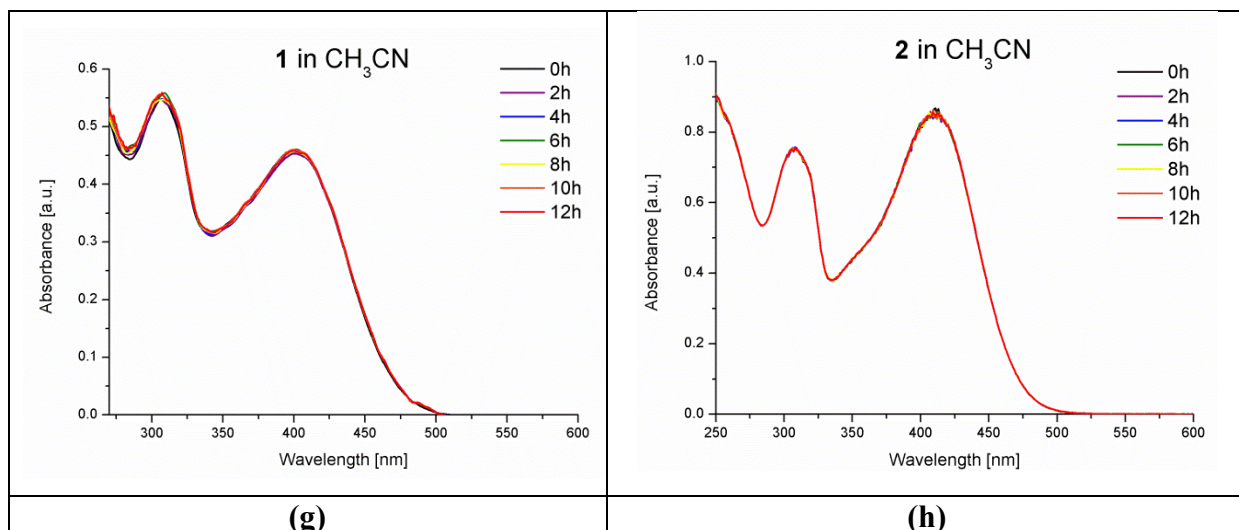


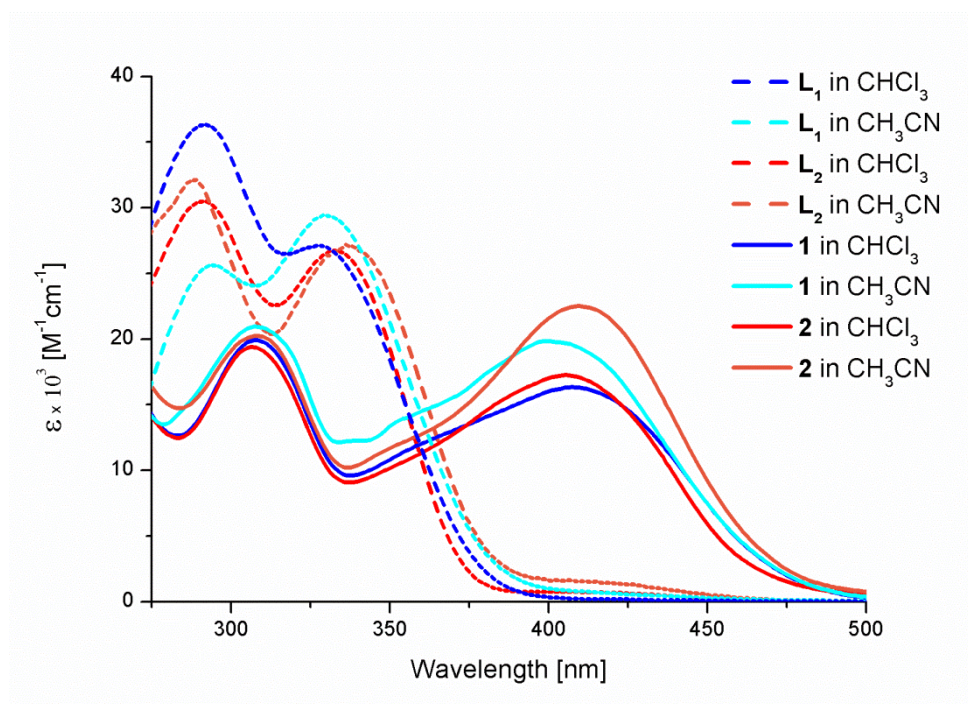
Figure S21. HMRS spectrum of **2**.

## UV-VIS studies

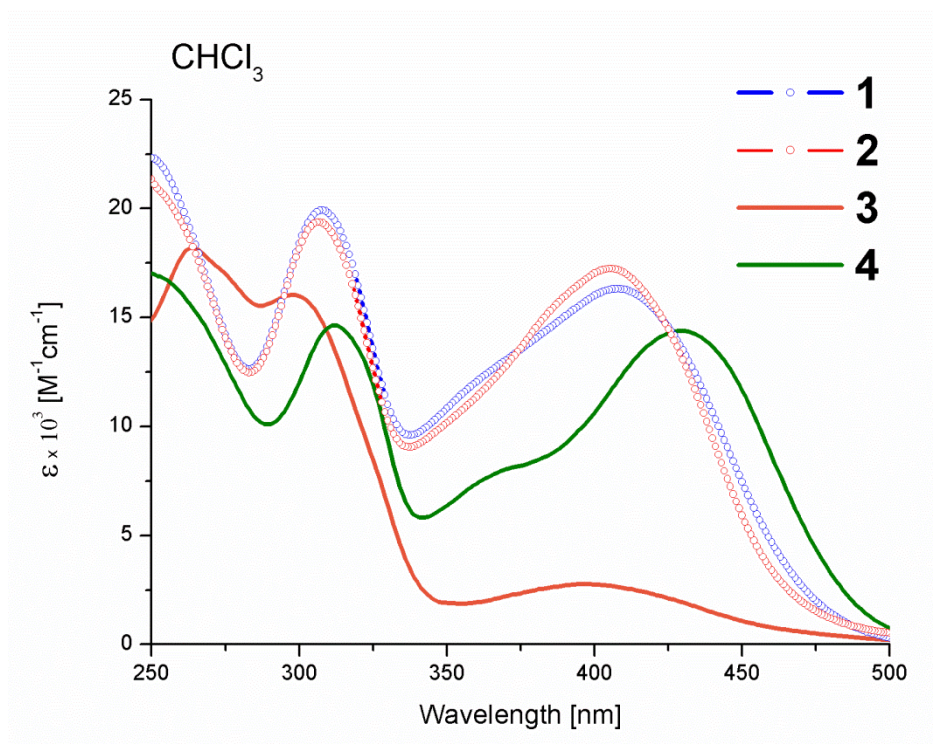




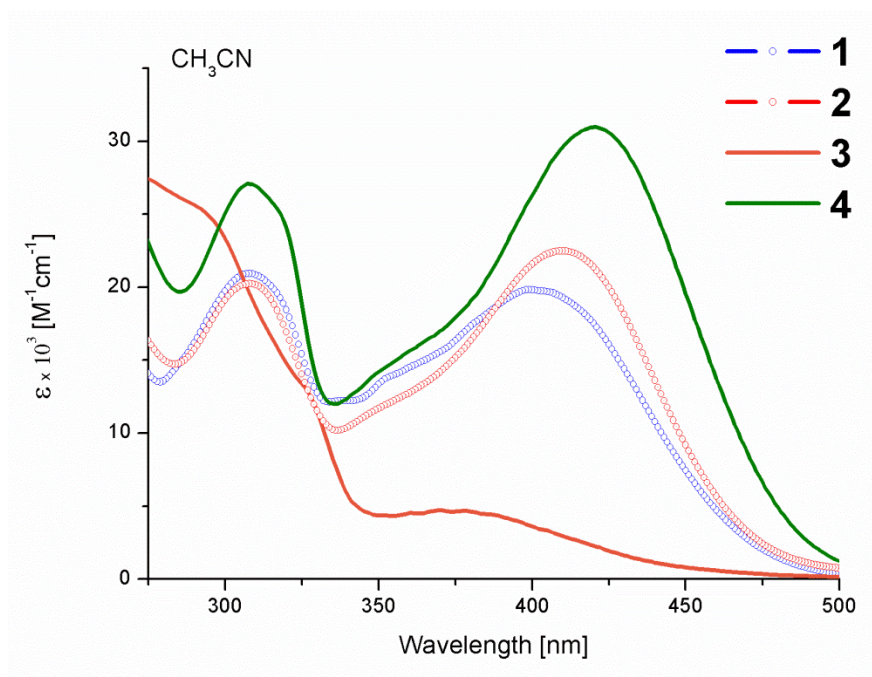
**Figure S22.** UV-Vis spectra of **1** and **2** in chloroform (a, b), tetrahydrofurane (c, d), N,N-dimethylformamide (e, f) and acetonitrile (g, h), recorded once every two hours over 12h at room temperature.



**Figure S23.** UV-Vis spectra of **1** and **2** in comparison to those for free ligands.



(a)



(b)

**Figure S24.** UV–Vis spectra of **1** and **2** in comparison to those for [ReCl(CO)<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>-terpy-κ<sup>2</sup>N)] (**3**) and [ReCl(CO)<sub>3</sub>(Me<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-terpy-κ<sup>2</sup>N)] (**4**) in CHCl<sub>3</sub> (a) and CH<sub>3</sub>CN (b).

**Table S6.** The absorption maxima and molar extinction coefficient for **1** and **2** with spectral data for [ReCl(CO)<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>-terpy-κ<sup>2</sup>N)] (**3**) and [ReCl(CO)<sub>3</sub>(Me<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-terpy-κ<sup>2</sup>N)] (**4**) chloroform (a), tetrahydrofuran (b), N,N-dimethylformamide (c) and acetonitrile (d).

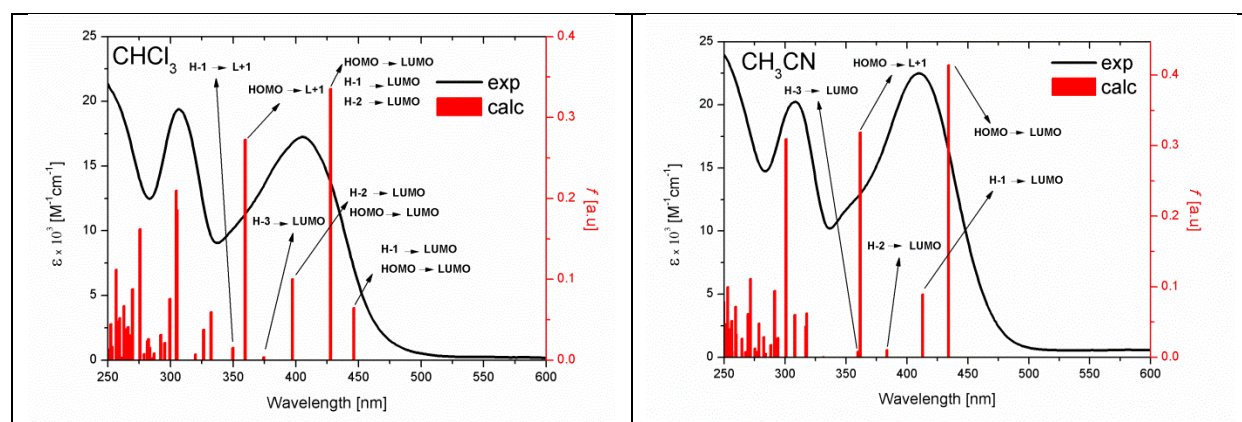
| Compound | $\lambda/\text{nm}$ ( $10^4 \epsilon/\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) |            |            |            |
|----------|------------------------------------------------------------------------------------------------|------------|------------|------------|
|          | CHCl <sub>3</sub>                                                                              | THF        | MeCN       | DMF        |
| <b>1</b> | 405 (1.63)                                                                                     | 405 (1.75) | 402 (1.93) | 409 (1.66) |
| <b>2</b> | 405 (1.72)                                                                                     | 406 (1.78) | 405 (2.24) | 417 (2.26) |
| <b>3</b> | 398 (0.27)                                                                                     | 400 (0.31) | 375 (0.46) | 385 (0.51) |
| <b>4</b> | 430 (1.44)                                                                                     | 415 (2.69) | 419 (1.65) | 425 (2.34) |

### Absorption properties - TDDFT calculations

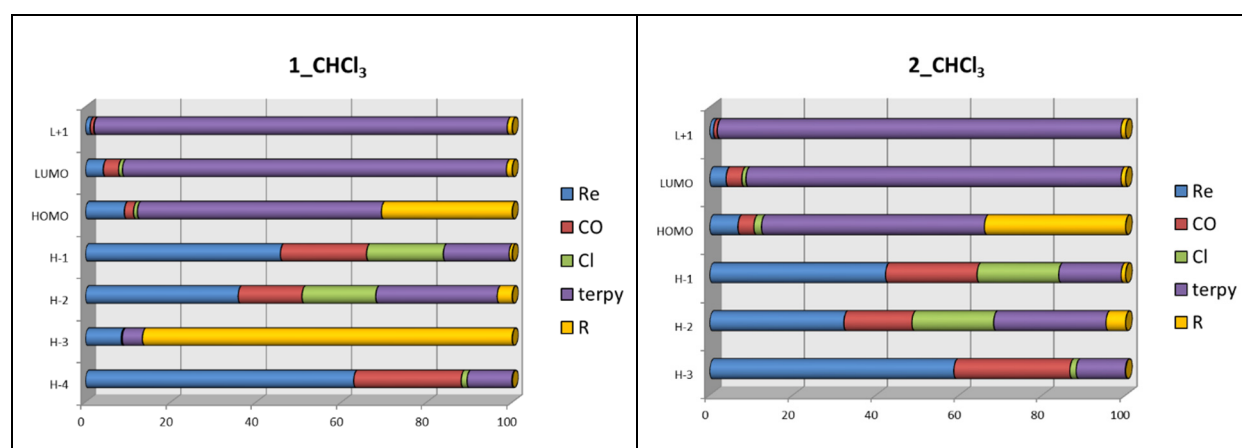
**Table S7.** The energies and characters of spin-allowed electronic transitions assigned to the lowest wavelength absorption bands of complexes **1** and **2** computed at the DFT/PBE1PBE/def2-TZVPD/def2-TZVP level.

| Compound<br>(medium)             | Experimental<br>absorption<br>$\lambda$ ; nm<br>( $10^4 \epsilon$ ; $\text{M}^{-1}\text{cm}^{-1}$ ) | Calculated transitions                                                                        |                          |           |                |                        |
|----------------------------------|-----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|--------------------------|-----------|----------------|------------------------|
|                                  |                                                                                                     | Major contribution (%)                                                                        | Predominant<br>character | E<br>[eV] | $\lambda$ [nm] | Oscillator<br>strength |
| <b>1</b><br>(CHCl <sub>3</sub> ) | 405 (1.89)                                                                                          | H-1 $\rightarrow$ LUMO (55%)<br>HOMO $\rightarrow$ LUMO (39%)                                 | MLCT<br>ILCT/IL          | 2.78      | 446.6          | 0.1234 $S_1$           |
|                                  |                                                                                                     | H-1 $\rightarrow$ LUMO (44%)<br>HOMO $\rightarrow$ LUMO (45%)                                 | MLCT<br>ILCT/IL          | 2.88      | 430.8          | 0.3347 $S_2$           |
|                                  |                                                                                                     | H-2 $\rightarrow$ LUMO (83%)<br>HOMO $\rightarrow$ LUMO (15%)                                 | MLCT<br>ILCT/IL          | 3.09      | 401.0          | 0.0496 $S_3$           |
|                                  |                                                                                                     | H-4 $\rightarrow$ LUMO (98%)                                                                  | MLCT                     | 3.32      | 373.6          | 0.0038 $S_4$           |
|                                  |                                                                                                     | HOMO $\rightarrow$ L+1 (95%)                                                                  | ILCT/IL                  | 3.41      | 363.9          | 0.3076 $S_5$           |
|                                  |                                                                                                     | H-1 $\rightarrow$ L+1 (96%)                                                                   | MLCT                     | 3.55      | 348.9          | 0.0042 $S_6$           |
| <b>1</b><br>(CH <sub>3</sub> CN) | 402 (2.87)                                                                                          | HOMO $\rightarrow$ LUMO (90%)                                                                 | ILCT/IL                  | 2.83      | 437.6          | 0.4426 $S_1$           |
|                                  |                                                                                                     | H-1 $\rightarrow$ LUMO (94%)                                                                  | MLCT                     | 2.99      | 414.0          | 0.0710 $S_2$           |
|                                  |                                                                                                     | H-3 $\rightarrow$ LUMO (84%)<br>H-2 $\rightarrow$ LUMO (11%)                                  | ILCT/IL<br>MLCT          | 3.22      | 384.8          | 0.0108 $S_3$           |
|                                  |                                                                                                     | HOMO $\rightarrow$ L+1 (96%)                                                                  | ILCT/IL                  | 3.41      | 363.3          | 0.3291 $S_4$           |
|                                  |                                                                                                     | H-4 $\rightarrow$ LUMO (97%)                                                                  | MLCT                     | 3.44      | 360.1          | 0.0045 $S_5$           |
| <b>2</b><br>(CHCl <sub>3</sub> ) | 405 (1.57)                                                                                          | H-1 $\rightarrow$ LUMO (65%)<br>HOMO $\rightarrow$ LUMO (30%)                                 | MLCT<br>ILCT/IL          | 2.78      | 446.4          | 0.0649 $S_1$           |
|                                  |                                                                                                     | HOMO $\rightarrow$ LUMO (48%)<br>H-1 $\rightarrow$ LUMO (34%)<br>H-2 $\rightarrow$ LUMO (17%) | ILCT/IL<br>MLCT<br>MLCT  | 2.90      | 427.8          | 0.3358 $S_2$           |
|                                  |                                                                                                     | H-2 $\rightarrow$ LUMO (76%)<br>HOMO $\rightarrow$ LUMO (21%)                                 | MLCT<br>ILCT/IL          | 3.12      | 397.4          | 0.1006 $S_3$           |
|                                  |                                                                                                     | H-3 $\rightarrow$ LUMO (98%)                                                                  | MLCT                     | 3.31      | 374.4          | 0.0039 $S_4$           |
|                                  |                                                                                                     | HOMO $\rightarrow$ L+1 (90%)                                                                  | ILCT/IL                  | 3.45      | 359.7          | 0.2728 $S_5$           |
|                                  |                                                                                                     | H-1 $\rightarrow$ L+1 (93%)                                                                   | MLCT                     | 3.55      | 349.7          | 0.0155 $S_6$           |
|                                  |                                                                                                     |                                                                                               |                          |           |                |                        |
| <b>2</b><br>(CH <sub>3</sub> CN) | 410 (2.69)                                                                                          | HOMO $\rightarrow$ LUMO (88%)                                                                 | ILCT/IL                  | 2.86      | 434.1          | 0.4142 $S_1$           |
|                                  |                                                                                                     | H-1 $\rightarrow$ LUMO (92%)                                                                  | MLCT                     | 3.00      | 413.0          | 0.0896 $S_2$           |
|                                  |                                                                                                     | H-2 $\rightarrow$ LUMO (94%)                                                                  | MLCT                     | 3.23      | 383.6          | 0.0108 $S_3$           |

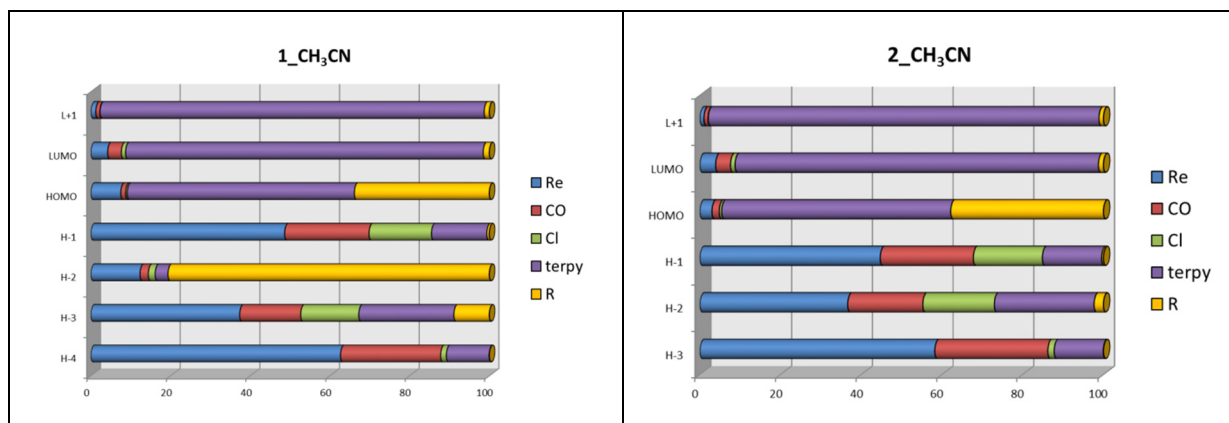
|  |  |                              |         |      |       |              |
|--|--|------------------------------|---------|------|-------|--------------|
|  |  | HOMO $\rightarrow$ L+1 (95%) | ILCT/IL | 3.43 | 361.6 | 0.3188 $S_4$ |
|  |  | H-3 $\rightarrow$ LUMO (96%) | MLCT    | 3.45 | 359.8 | 0.0084 $S_5$ |



**Figure S25.** Experimental (black line) absorption spectra of **2** alongside red vertical lines presenting singlet-singlet transitions with corresponding oscillator strengths, computed at TD-DFT/PCM/PBE1PBE/def2-TZVPD/def2-TZVP level with the use of the PCM model at polarities corresponding to MeCN and  $\text{CHCl}_3$ .



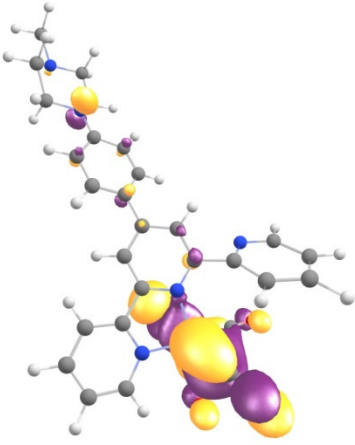
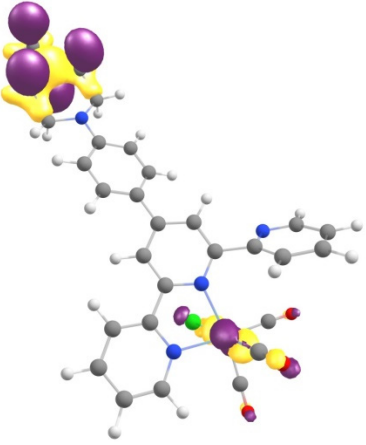
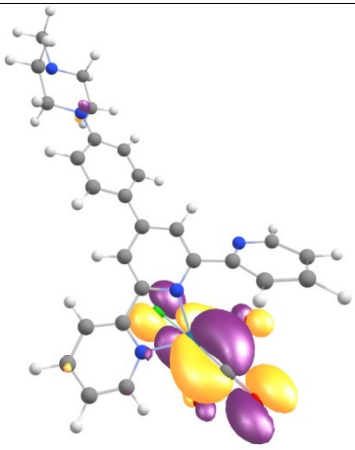
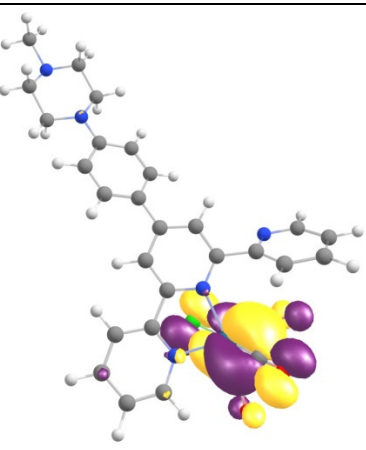
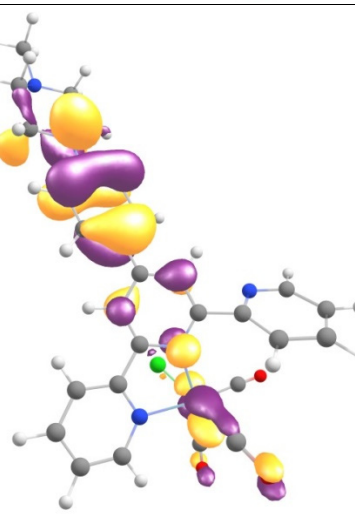
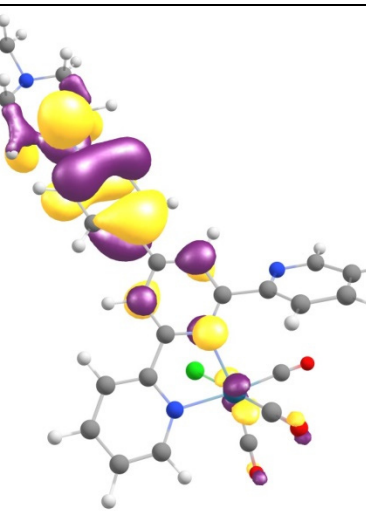
**Figure S26.** Percentage composition of molecular orbitals for **1** and **2** (in  $\text{CHCl}_3$ ) computed at the DFT/PBE1PBE/def2-TZVPD/def2-TZVP level.

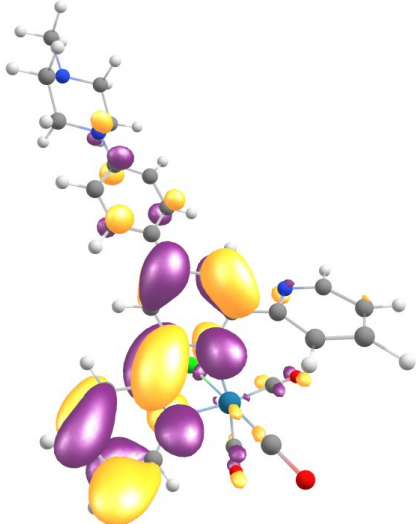
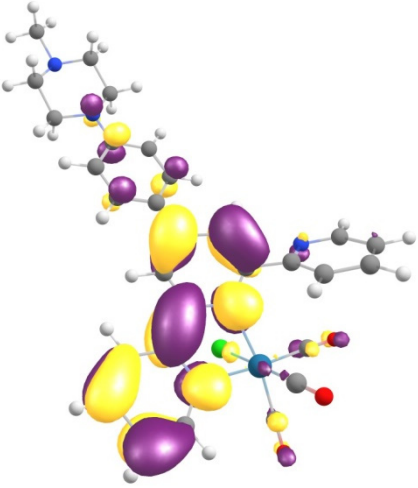
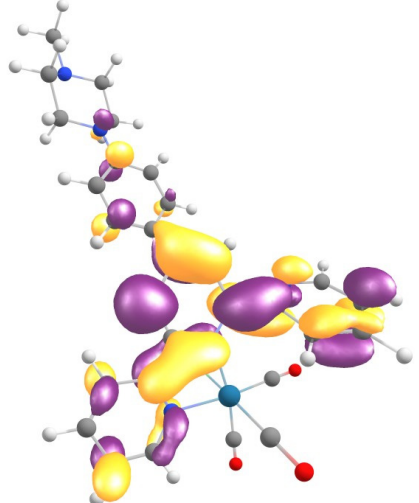
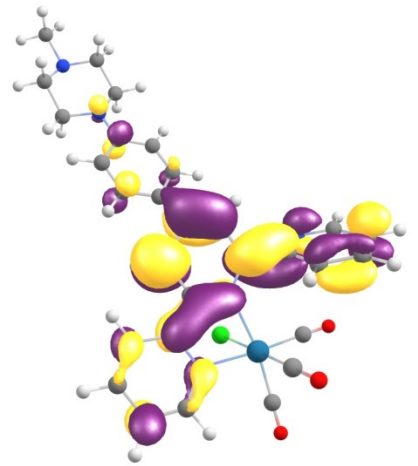


**Figure S27.** Percentage composition of molecular orbitals for **1** and **2** (in CH<sub>3</sub>CN) computed at the DFT/PBE1PBE/def2-TZVPD/def2-TZVP level.

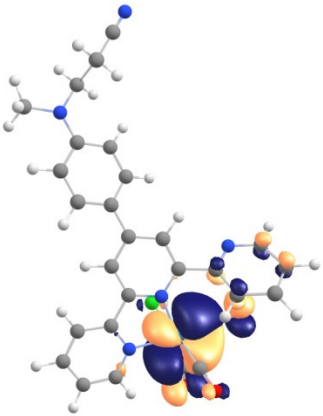
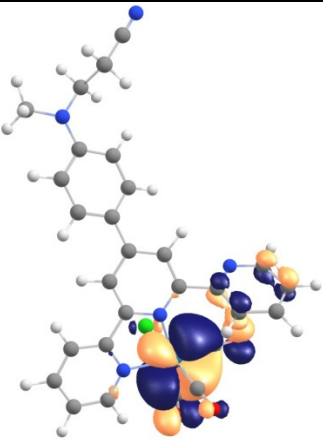
**Table S8.** Selected molecular orbitals of **1** computed at the DFT/PBE1PBE/def2-TZVPD/def2-TZVP level.

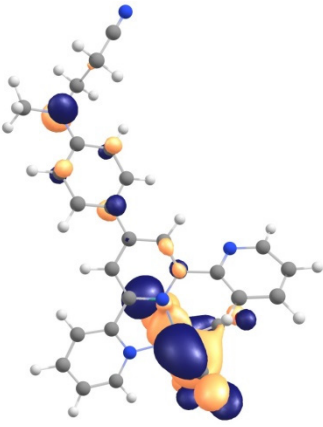
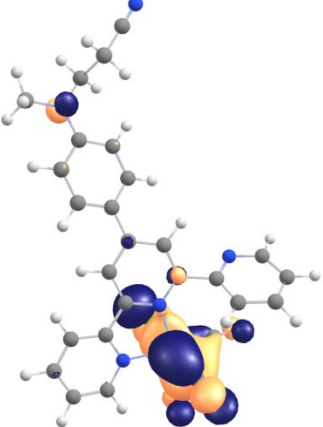
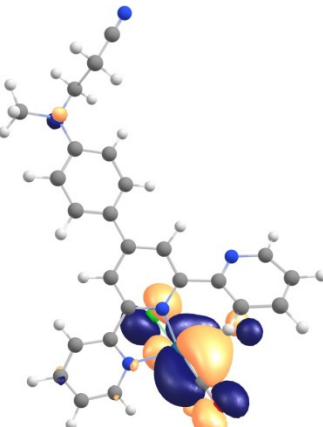
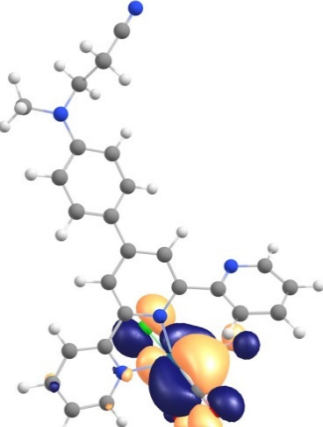
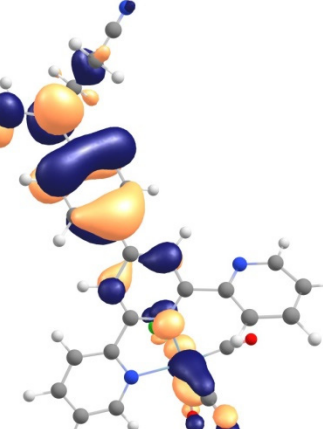
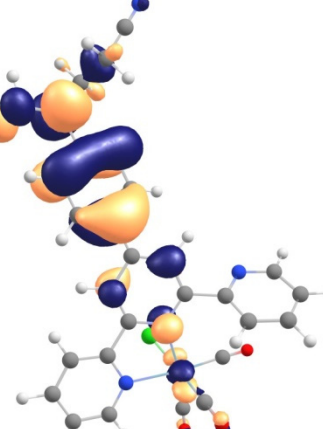
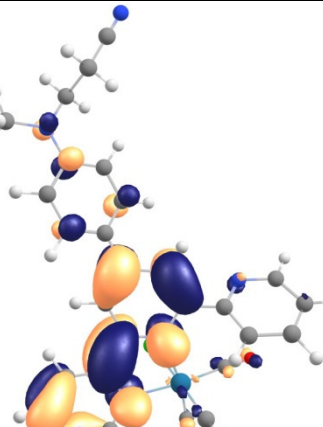
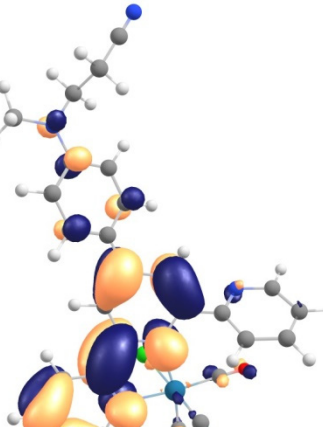
|     | CHCl <sub>3</sub> | CH <sub>3</sub> CN |
|-----|-------------------|--------------------|
| H-4 |                   |                    |
| H-3 |                   |                    |

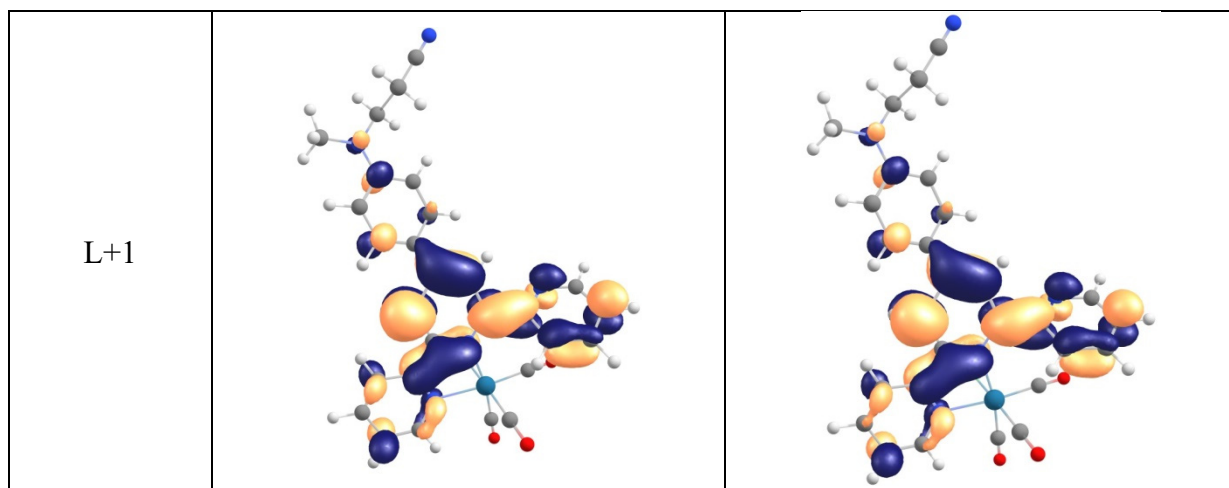
|      |                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                               |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| H-2  |  <p>Left view of the H-2 molecular orbital. The molecule is shown with carbon in grey, nitrogen in blue, and oxygen in red. The orbital is represented by yellow and purple isosurfaces, with a large purple lobe on the right side of the molecule.</p>    |  <p>Right view of the H-2 molecular orbital. The molecule is shown with carbon in grey, nitrogen in blue, and oxygen in red. The orbital is represented by yellow and purple isosurfaces, with a large purple lobe on the left side of the molecule.</p>    |
| H-1  |  <p>Left view of the H-1 molecular orbital. The molecule is shown with carbon in grey, nitrogen in blue, and oxygen in red. The orbital is represented by yellow and purple isosurfaces, with a large purple lobe on the right side of the molecule.</p>   |  <p>Right view of the H-1 molecular orbital. The molecule is shown with carbon in grey, nitrogen in blue, and oxygen in red. The orbital is represented by yellow and purple isosurfaces, with a large purple lobe on the left side of the molecule.</p>   |
| HOMO |  <p>Left view of the HOMO molecular orbital. The molecule is shown with carbon in grey, nitrogen in blue, and oxygen in red. The orbital is represented by yellow and purple isosurfaces, with a large purple lobe on the right side of the molecule.</p> |  <p>Right view of the HOMO molecular orbital. The molecule is shown with carbon in grey, nitrogen in blue, and oxygen in red. The orbital is represented by yellow and purple isosurfaces, with a large purple lobe on the left side of the molecule.</p> |

|      |                                                                                    |                                                                                     |
|------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| LUMO |   |   |
| L+1  |  |  |

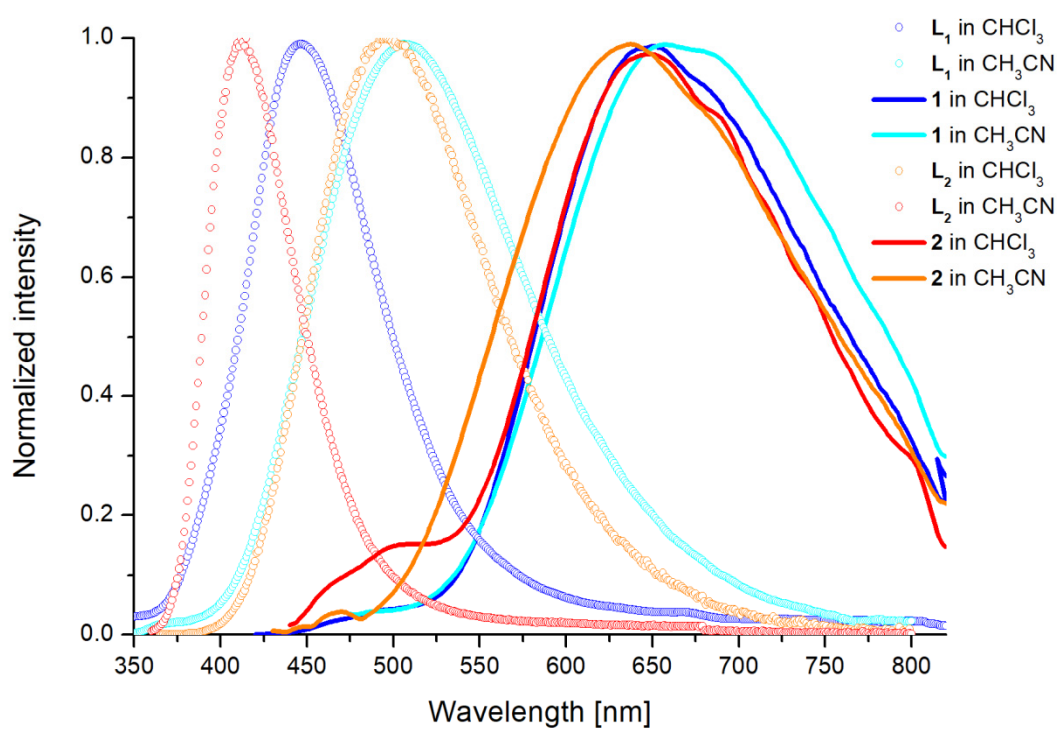
**Table S9.** Selected molecular orbitals of **2** computed at the DFT/PBE1PBE/def2-TZVPD/def2-TZVP level.

|     | CHCl <sub>3</sub>                                                                   | CH <sub>3</sub> CN                                                                   |
|-----|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| H-3 |  |  |

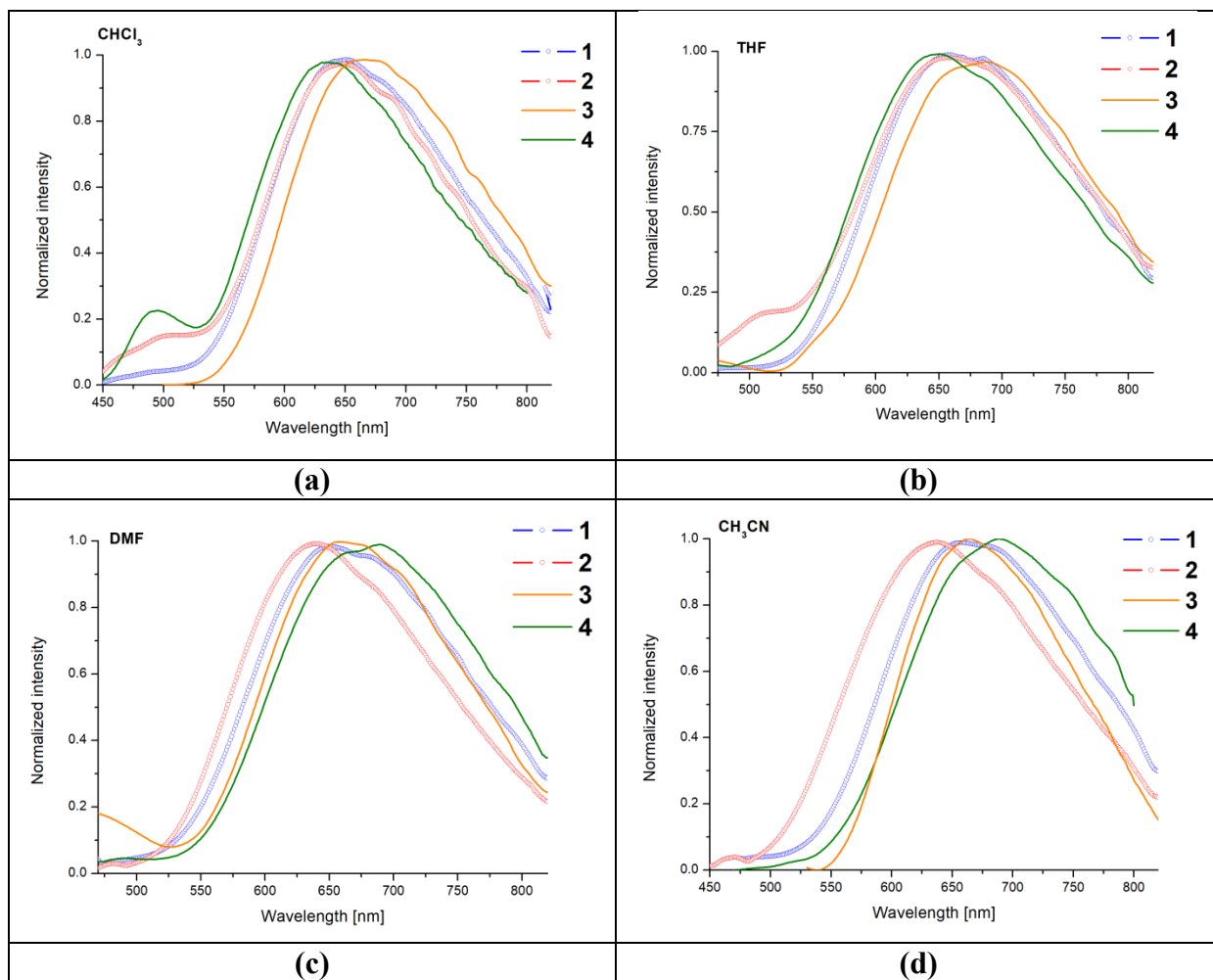
|      |                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                            |
|------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| H-2  |  Molecular orbital visualization for H-2, left view. The molecule is shown with blue and orange isosurfaces representing the orbital density. The structure is a complex organic molecule with multiple rings and functional groups.    |  Molecular orbital visualization for H-2, right view. The molecule is shown with blue and orange isosurfaces representing the orbital density. The structure is a complex organic molecule with multiple rings and functional groups.    |
| H-1  |  Molecular orbital visualization for H-1, left view. The molecule is shown with blue and orange isosurfaces representing the orbital density. The structure is a complex organic molecule with multiple rings and functional groups.   |  Molecular orbital visualization for H-1, right view. The molecule is shown with blue and orange isosurfaces representing the orbital density. The structure is a complex organic molecule with multiple rings and functional groups.   |
| HOMO |  Molecular orbital visualization for HOMO, left view. The molecule is shown with blue and orange isosurfaces representing the orbital density. The structure is a complex organic molecule with multiple rings and functional groups. |  Molecular orbital visualization for HOMO, right view. The molecule is shown with blue and orange isosurfaces representing the orbital density. The structure is a complex organic molecule with multiple rings and functional groups. |
| LUMO |  Molecular orbital visualization for LUMO, left view. The molecule is shown with blue and orange isosurfaces representing the orbital density. The structure is a complex organic molecule with multiple rings and functional groups. |  Molecular orbital visualization for LUMO, right view. The molecule is shown with blue and orange isosurfaces representing the orbital density. The structure is a complex organic molecule with multiple rings and functional groups. |



### Photoluminescence studies



**Figure S28.** Normalized emission spectra of **1** and **2** in comparison to those for free ligands



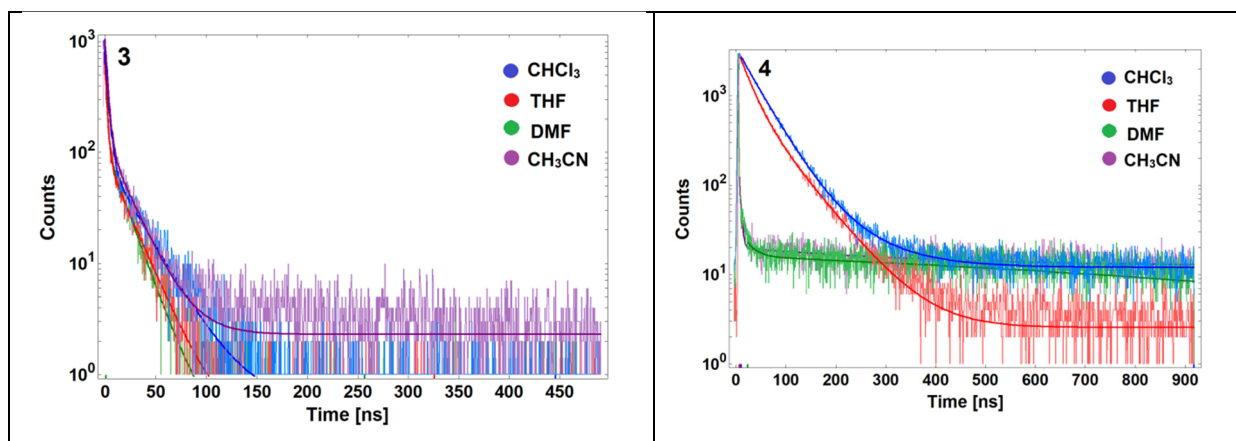
**Figure S29.** Normalized luminescence spectra of **1–4** in deaerated chloroform (a), tetrahydrofuran (b), N,N–dimethylformamide (c) and acetonitrile (d).

**Table S10.** Relevant photophysical parameters of **1** and **2** in comparison to those for [ReCl(CO)<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>-terpy-κ<sup>2</sup>N)] (**3**) and [ReCl(CO)<sub>3</sub>(Me<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-terpy-κ<sup>2</sup>N)] (**4**).

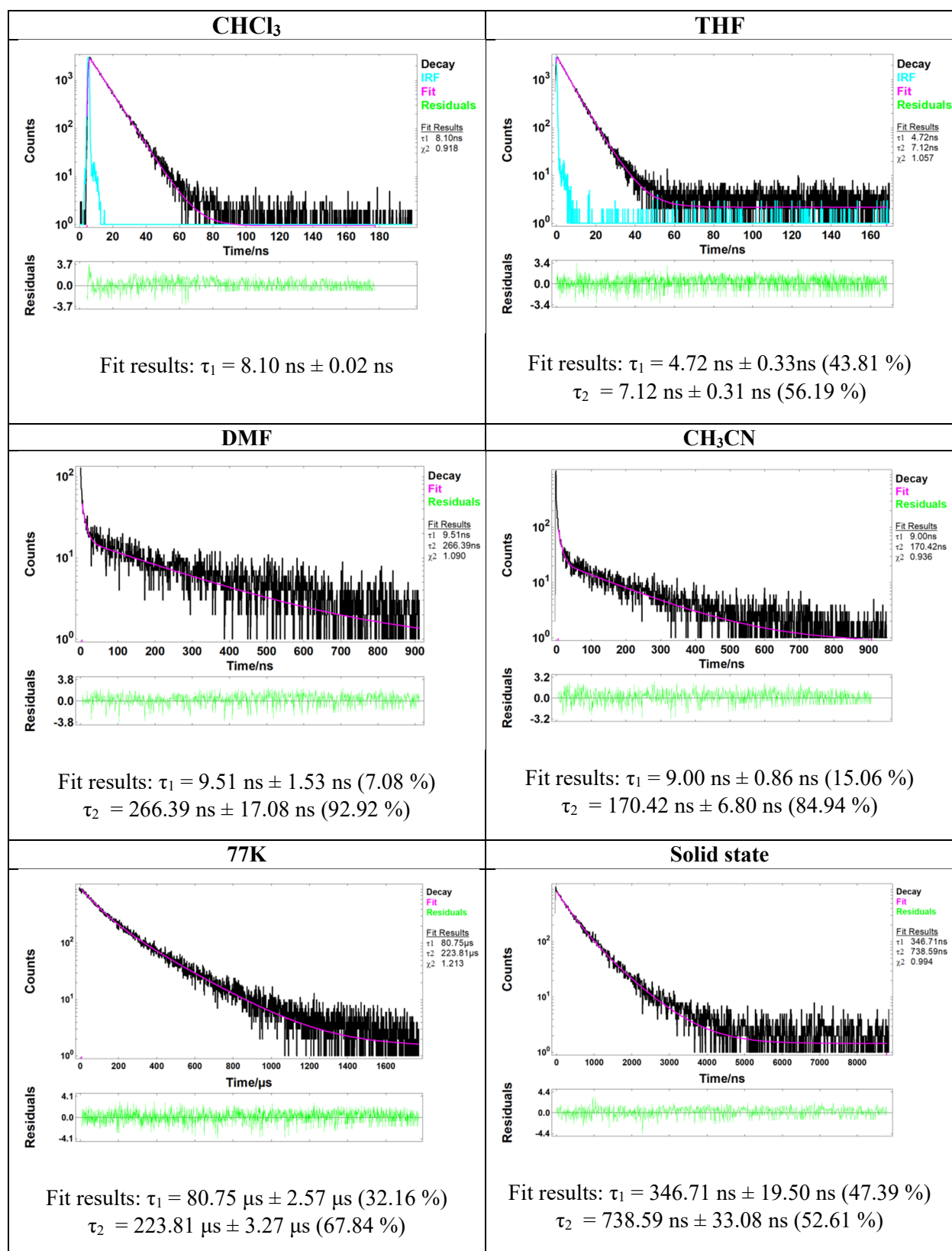
| Compound | Medium             | $\lambda_{\text{ex}}$<br>[nm] | $\lambda_{\text{em}}$<br>[nm] | Stokes<br>shift<br>[cm <sup>-1</sup> ] | $\tau$                                          | $\tau_{\text{av}}$ | $\Phi$ |
|----------|--------------------|-------------------------------|-------------------------------|----------------------------------------|-------------------------------------------------|--------------------|--------|
| <b>1</b> | CHCl <sub>3</sub>  | 405                           | 645                           | 9190                                   | 8.10 ns                                         | 8.10 ns            | 0.009  |
|          | THF                | 405                           | 665                           | 9840                                   | 4.72 ns (43.81%) 7.12 ns (56.19)                | 6.07 ns            | 0.01   |
|          | DMF                | 409                           | 650                           | 9060                                   | 9.51 ns (7.08%), 266.39 ns (92.92%)             | 248.20 ns          | 0.001  |
|          | CH <sub>3</sub> CN | 405                           | 665                           | 9650                                   | 9.00 ns (15.06%), 170.42 ns (84.94%)            | 146.11 ns          | <0.001 |
|          | 77K<br>(EtOH-MeOH) | 420                           | 560                           | 5950                                   | 80.75 $\mu$ s (32.16%), 223.81 $\mu$ s (67.84%) | 177.80 $\mu$ s     | –      |
|          | solid              | 475                           | 613                           | 4740                                   | 346.71 ns (47.39%), 738.59 ns (52.61%)          | 552.88 ns          | 0.071  |
| <b>2</b> | CHCl <sub>3</sub>  | 430                           | 643                           | 7700                                   | 7.36 ns (98.0%), 30.49 ns (1.96 %)              | 7.81 ns            | 0.026  |
|          | THF                | 445                           | 665                           | 7430                                   | 5.40 ns (97.52%), 29.01 ns (2.48)               | 5.99 ns            | 0.027  |

|                                                                                                          |                    |     |             |       |                                        |           |        |
|----------------------------------------------------------------------------------------------------------|--------------------|-----|-------------|-------|----------------------------------------|-----------|--------|
|                                                                                                          | DMF                | 420 | 640         | 8180  | 100.69 ns (19.67%), 696.39 ns (80.33%) | 579.22 ns | 0.003  |
|                                                                                                          | CH <sub>3</sub> CN | 415 | 640         | 8470  | 11.27 (18.65%), 100.42 (76.38%)        | 78.80 ns  | 0.003  |
|                                                                                                          | 77K<br>(EtOH-MeOH) | 410 | 564         | 6660  | 75.46 μs (28.46%), 211.490 μs (71.54%) | 172.76 μs | –      |
|                                                                                                          | solid              | 450 | 560,589,649 | 6810  | 326.31 ns (39.61%), 1157.5 ns (60.39%) | 828.27 ns | 0.003  |
| [ReCl(CO) <sub>3</sub> (Ph-terpy)]<br>(3)                                                                | CHCl <sub>3</sub>  | 400 | 667         | 10010 | 3.27 ns (71.01%), 28.45ns (28.99%)     | 10.57 ns  | 0.004* |
|                                                                                                          | THF                | 400 | 676         | 10210 | 1.98 ns (61.56%), 19.52 ns (38.44%)    | 8.72 ns   | 0.002  |
|                                                                                                          | DMF                | 385 | 665         | 10940 | 1.77 ns (56.75%), 16.61 ns (43.25%)    | 7.18 ns   | 0.002  |
|                                                                                                          | CH <sub>3</sub> CN | 380 | 666         | 11300 | 2.18 ns (71.42%), 16.01 ns (28.58%)    | 6.13 ns   | 0.002  |
|                                                                                                          | 77K<br>(EtOH-MeOH) | 384 | 543         | 7630  | 2.28 μs (22.41%), 5.88 μs (77.59%)     | 5.07 μs   | –      |
|                                                                                                          | solid              | 442 | 592         | 5730  | 30.04 ns (65.78%), 94.89 ns (34.22%)   | 52.23 ns  | 0.012  |
| [ReCl(CO) <sub>3</sub> ((CH <sub>3</sub> ) <sub>2</sub> -N-C <sub>6</sub> H <sub>4</sub> -terpy)]<br>(4) | CHCl <sub>3</sub>  | 425 | 637         | 7830  | 17.4 ns (94.4%), 63.9 ns (5.6%)        | 20.00 ns  | 0.013  |
|                                                                                                          | THF                | 415 | 650         | 8710  | 23.1 ns (42.54%), 64.08 ns(57.46%)     | 46.64 ns  | 40.045 |
|                                                                                                          | DMF                | 425 | 680         | 7520  | 27.44 ns (1.28%), 1696.08 ns (98.72%)  | 1.67 μs   | <0.001 |
|                                                                                                          | CH <sub>3</sub> CN | 456 | 687         | 7370  | 2.65ns (10.03%), 197.12 ns (89.97%)    | 177.60 ns | 0.020  |
|                                                                                                          | 77K<br>(EtOH-MeOH) | 444 | 580         | 5280  | 263.0 μs (77.9%), 103.0 μs (22.1%)     | 227.64 μs | –      |
|                                                                                                          | solid              | 494 | 636         | 4520  | 0.3 μs (61.8%), 3.1 μs (38.2%)         | 1.37 μs   | 0.007  |

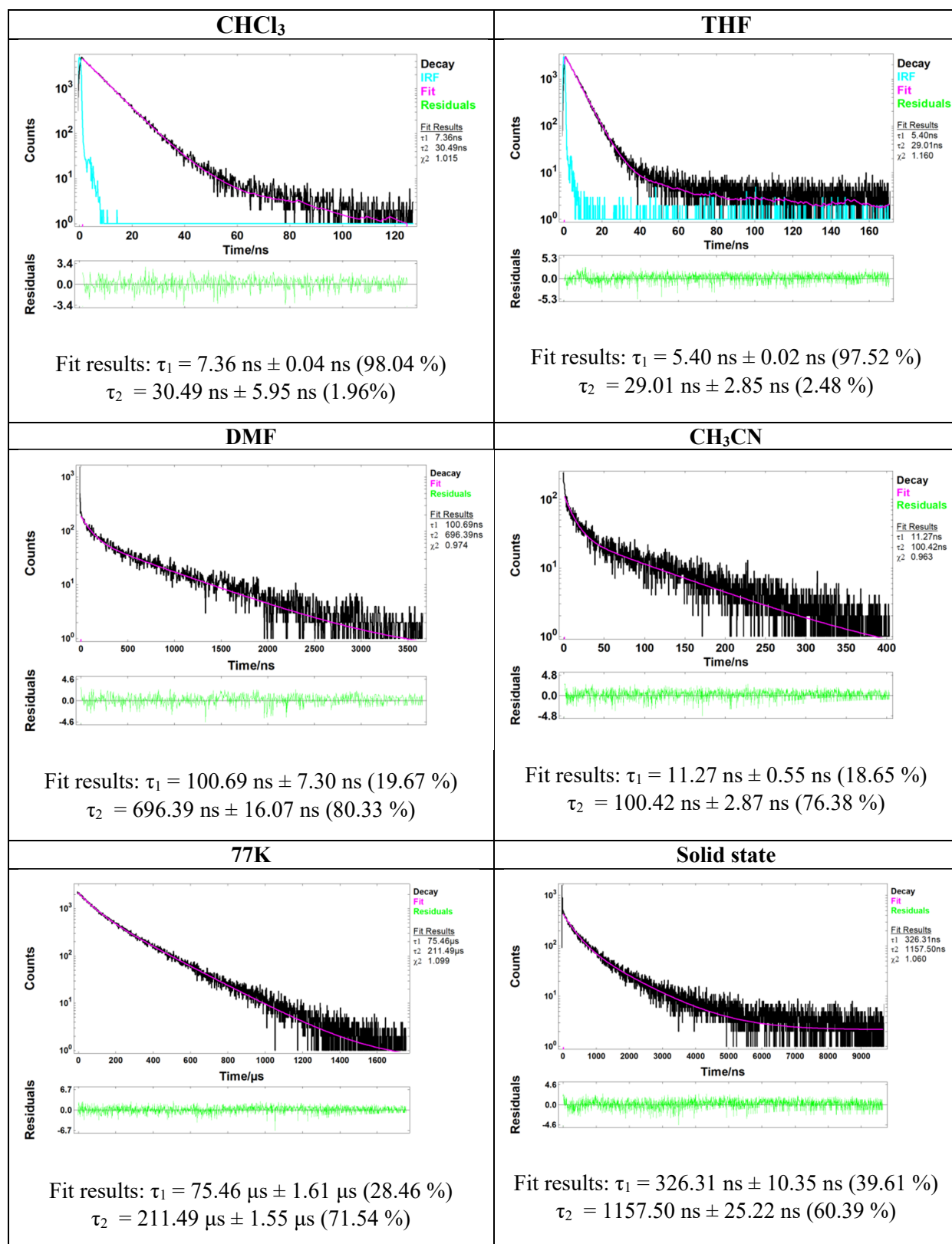
\* Klemens, T.; Świtlicka, A.; Szlapa-Kula, A.; Krompiec, S.; Lodowski, P.; Chrobok, A.; Godlewska, M.; Kotowicz, S.; Siwy, M.; Bednarczyk, K.; et al. Experimental and Computational Exploration of Photophysical and Electroluminescent Properties of Modified 2,2':6',2''-Terpyridine, 2,6-Di(Thiazol-2-Yl)Pyridine and 2,6-Di(Pyrazin-2-Yl)Pyridine Ligands and Their Re(I) Complexes. *Appl. Organomet. Chem.* **2018**, 32, e4611, doi:10.1002/aoc.4611.



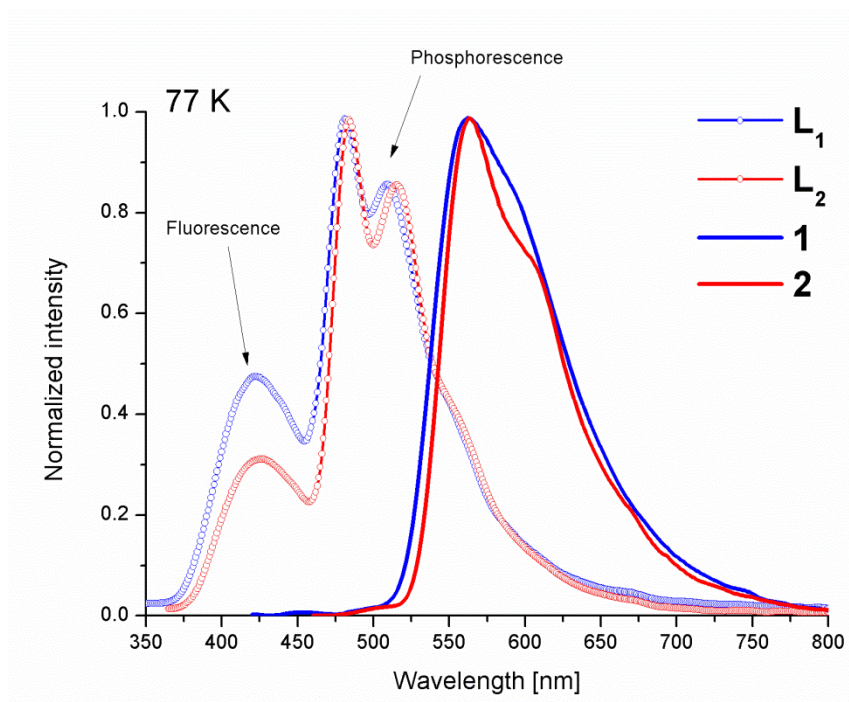
**Figure S30.** TCSPC decay curves for **3** and **4** in different solvents.



**Figure S31.** Decay curves of **1** in deaerated CHCl<sub>3</sub>, THF, DMF, CH<sub>3</sub>CN at room temperature, in ethanol-methanol rigid-glass matrix (77 K) and solid state.



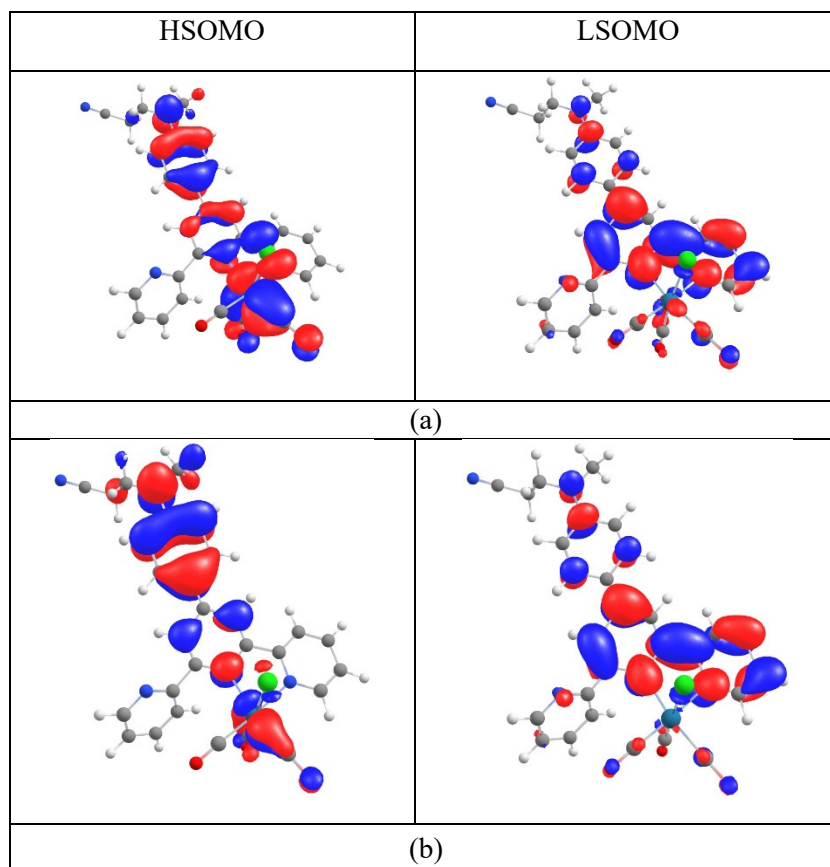
**Figure S32.** Decay curves of **2** in deaerated CHCl<sub>3</sub>, THF, DMF, CH<sub>3</sub>CN at room temperature, in ethanol-methanol rigid-glass matrix (77 K) and solid state.



**Figure S33.** Normalized emission spectra of the free ligands and their Re(I) complexes in ethanol-methanol rigid-glass matrix (77 K). The emission spectra of the free ligands were recorded with the addition of 10% ethyl iodide. The highest energy band in the emission spectra of the free ligands corresponds to the unquenched fluorescence.

**Table S11.** Calculated phosphorescence emission energies (DFT/PBE1PBE/def2-TZVPD/def2-TZVP) of **1** and **2**, compared to the experimental values recorded in acetonitrile solution.

| Compound                       | TD-DFT             |        |                             |                  | $\lambda_{\text{exp}}$<br>[eV/nm] |
|--------------------------------|--------------------|--------|-----------------------------|------------------|-----------------------------------|
|                                | Major contribution | E [eV] | $\lambda_{\text{cal}}$ [nm] | Character        |                                   |
| <b>1</b><br>CHCl <sub>3</sub>  | H→L (84%)          | 1.88   | 659                         | ILCT/IL and MLCT | 1.93/642                          |
| <b>1</b><br>CH <sub>3</sub> CN | H→L (86%)          | 1.89   | 657                         | ILCT/IL and MLCT | 1.86/665                          |
| <b>2</b><br>CHCl <sub>3</sub>  | H→L (94%)          | 1.73   | 718                         | ILCT/IL and MLCT | 1.93/643                          |
| <b>2</b><br>CH <sub>3</sub> CN | H→L (85%)          | 1.96   | 631                         | ILCT/IL and MLCT | 1.94/640                          |

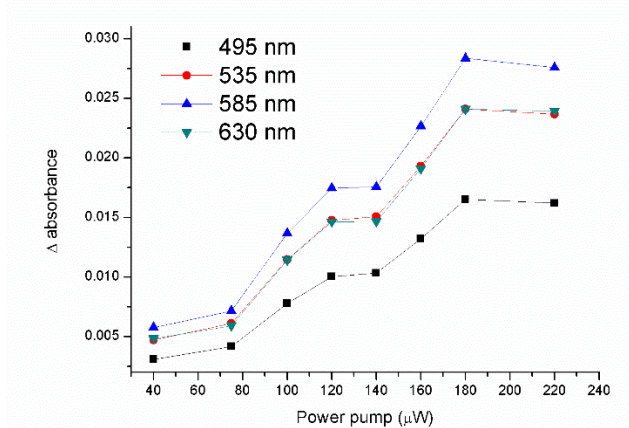


**Figure S34.** Representative isodensity surface plots of the LSOMO and HSOMO for complex **2** (TD-DFT at  $T_1$  state geometry, red and blue colors show regions of excess  $\alpha$  spin density and excess  $\beta$  spin density values, respectively), as well as the spin density surface plots (DFT,  $T_1$  state geometry; green and blue colors show regions of excess  $\alpha$  spin density and excess  $\beta$  spin density values, respectively) simulated with the PCM model in chloroform (a) and acetonitrile (b).

## Femtosecond transient absorption spectroscopy

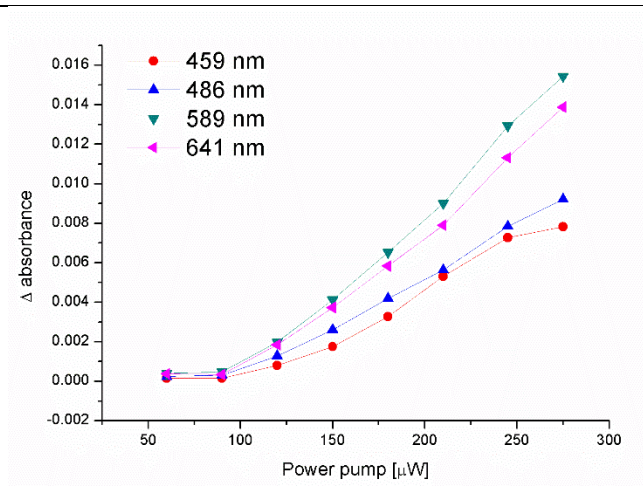
### **1** in CH<sub>3</sub>CN

Fluence test was performed at 20 ps time delay, in the range 40 to 220  $\mu$ W. Compound **1** showed a linear regime within range 40–100  $\mu$ W. The fsTA measurement of **1** was carried out at 70  $\mu$ W, approaching the highest value of power pump within the linear range.



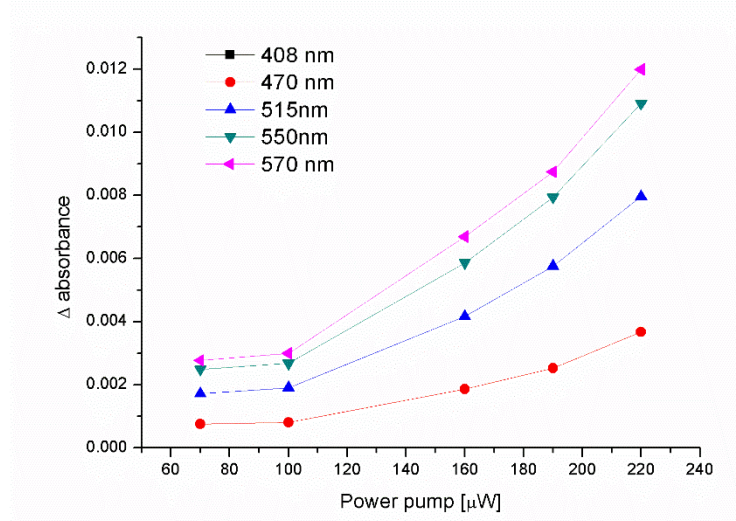
### **1** in CHCl<sub>3</sub>

Fluence test was performed at 20 ps time delay, in the range 40 to 250  $\mu$ W. Compound **1** showed a linear regime within range 40–90  $\mu$ W. The fsTA measurement of **1** was performed at a value of 70  $\mu$ W, which is in the linear range.



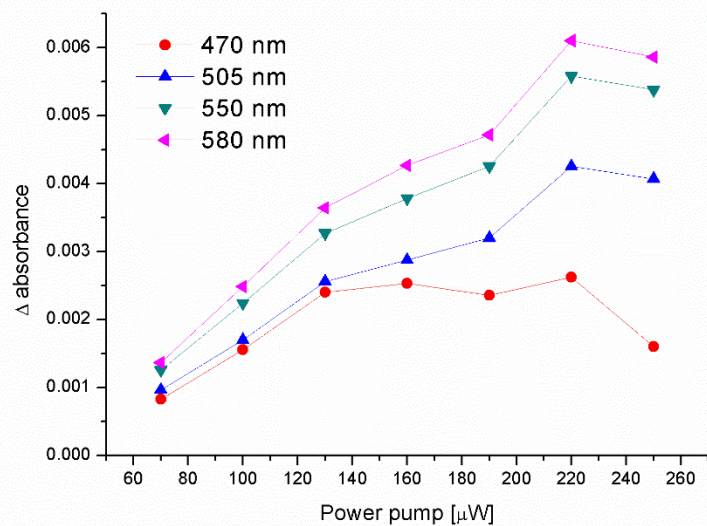
### **2** in $\text{CH}_3\text{CN}$

Fluence test was performed at 20 ps time delay, in the range 70 to 220  $\mu$ W. Compound **2** showed a linear regime within range 70-160  $\mu$ W. The fsTA measurement of **2** was performed at a value of 120  $\mu$ W, which is in the linear range



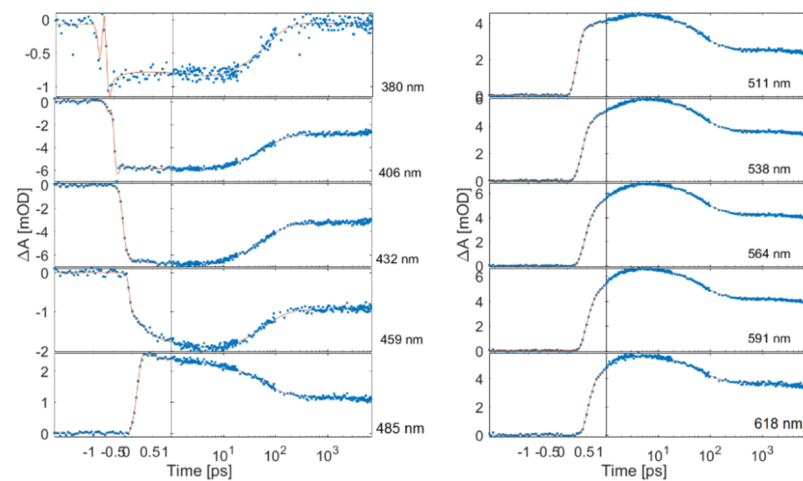
### **2** in $\text{CHCl}_3$

Fluence test was performed at 20 ps time delay, in the range 70 to 220  $\mu\text{W}$ . Compound **2** showed a linear regime within range 70-130  $\mu\text{W}$ . The fsTA measurement of **2** was performed at a value of 130  $\mu\text{W}$ , which is in the linear range.

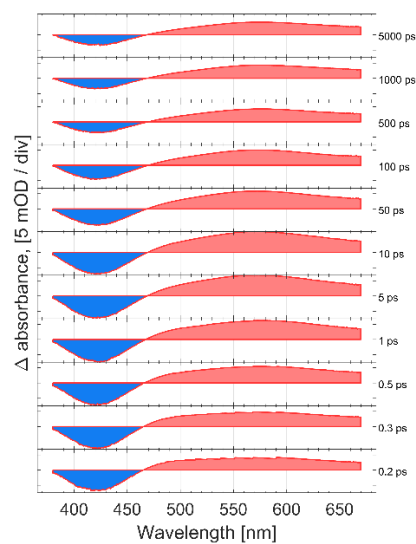
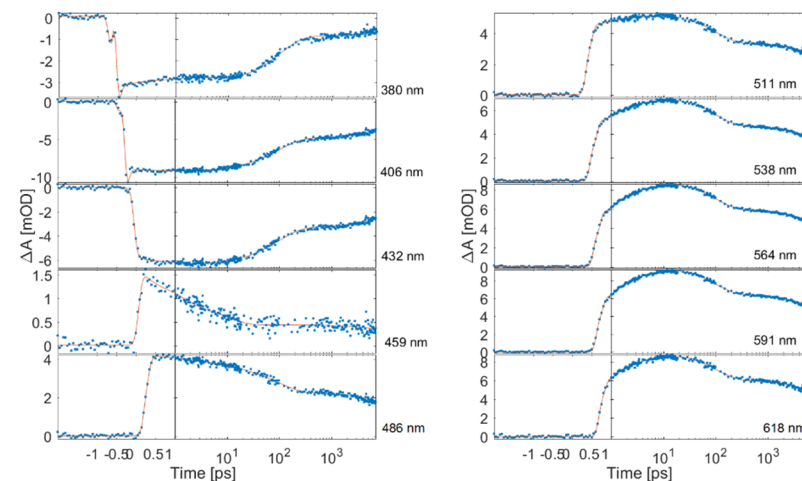


**Figure S35.** The results of fluence dependence of **1** and **2**.

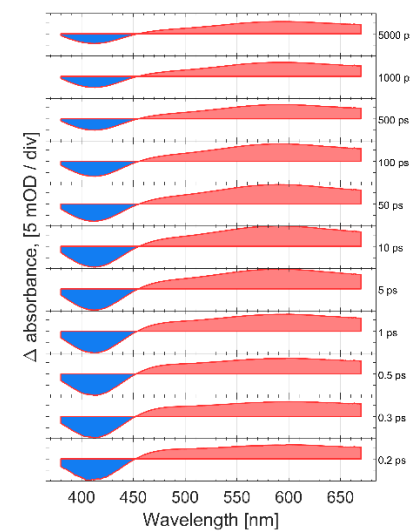
**1 in CH<sub>3</sub>CN**



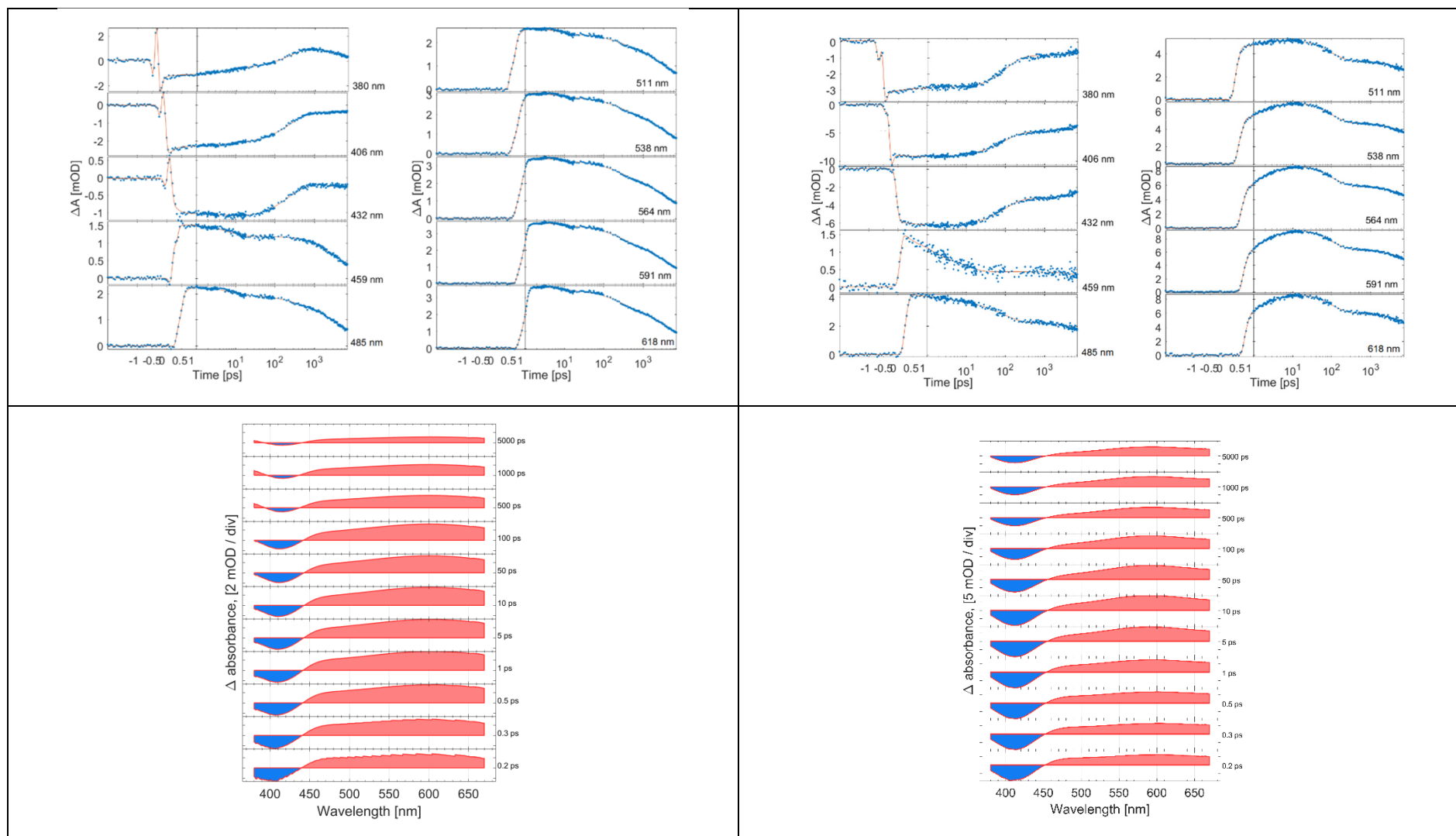
**2 in CH<sub>3</sub>CN**



**1 in CHCl<sub>3</sub>**

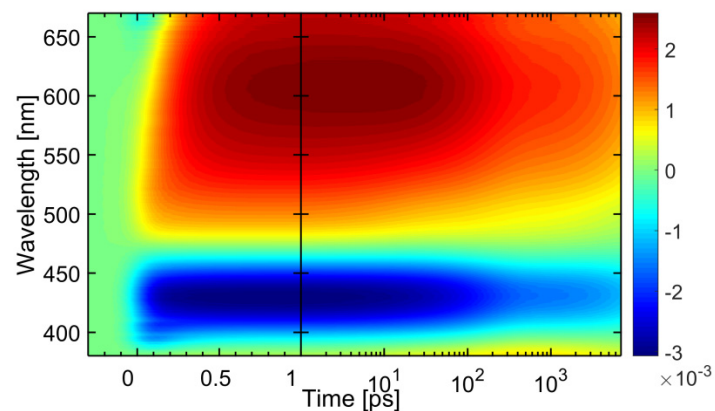


**2 in CHCl<sub>3</sub>**

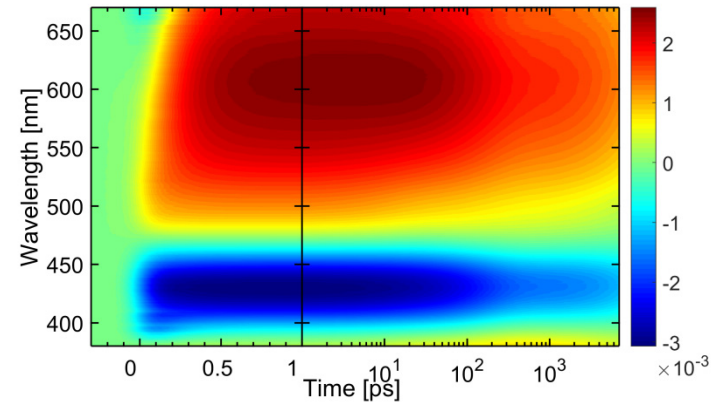


**Figure 36.** TA spectra at selected time delays and time traces at several wavelength for **1** and **2** in chloroform and acetonitrile.

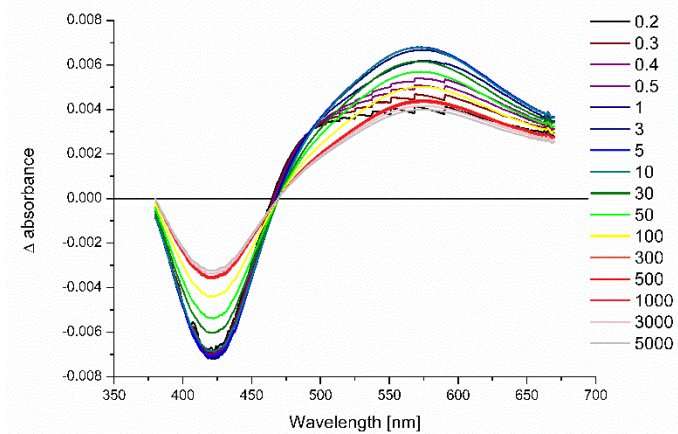
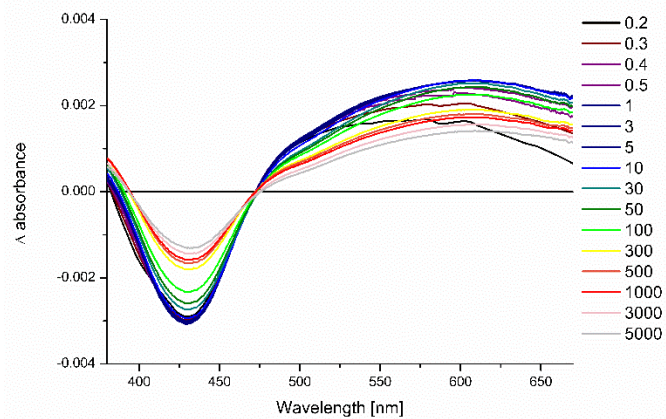
**4 in CHCl<sub>3</sub>**



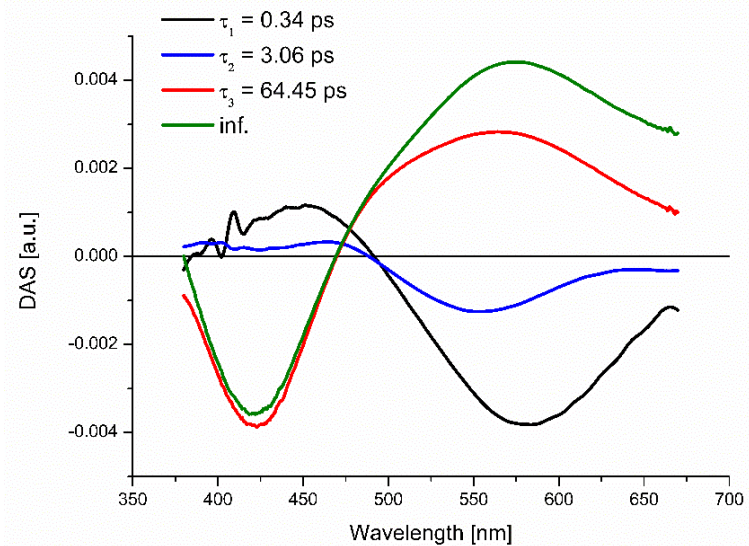
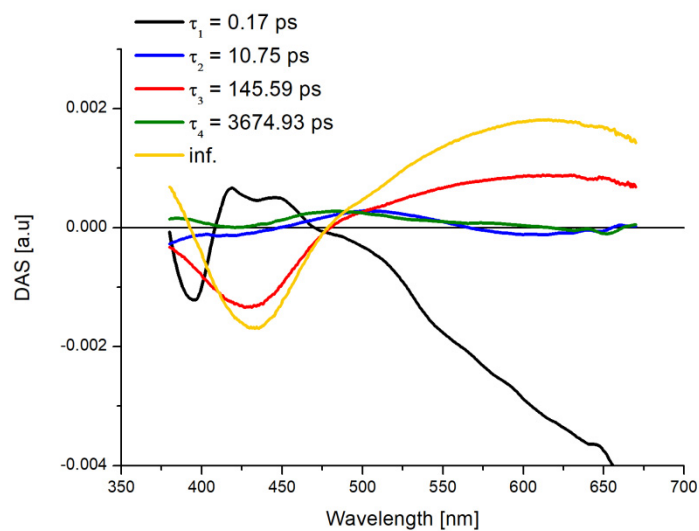
**4 in CH<sub>3</sub>CN**



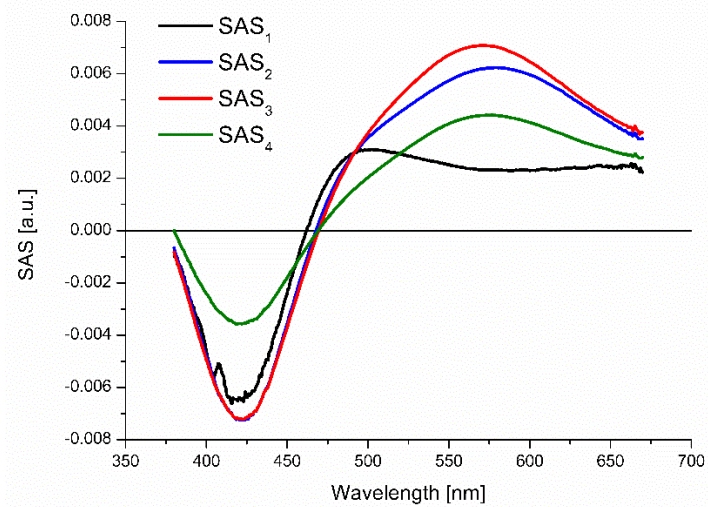
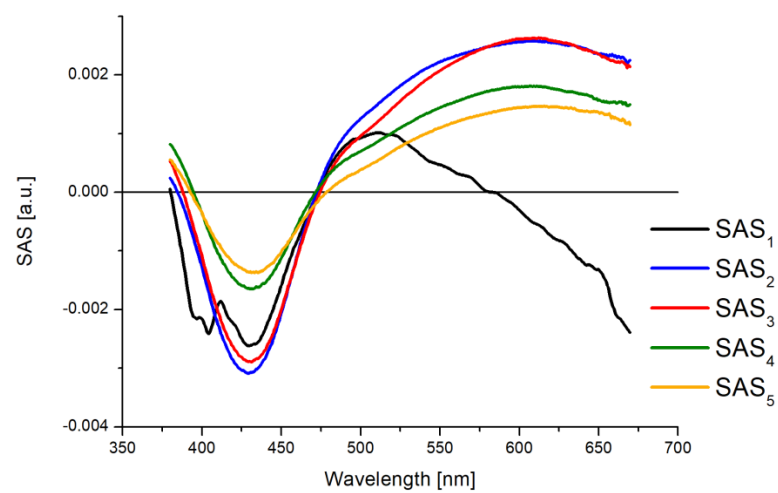
**(a)**



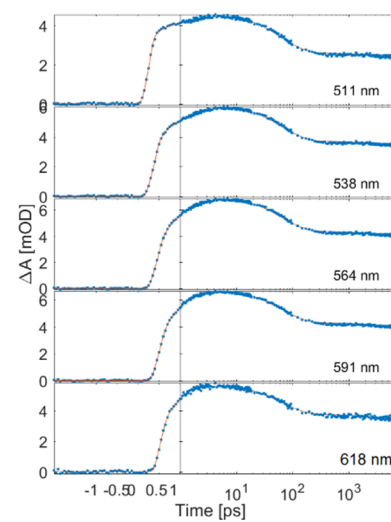
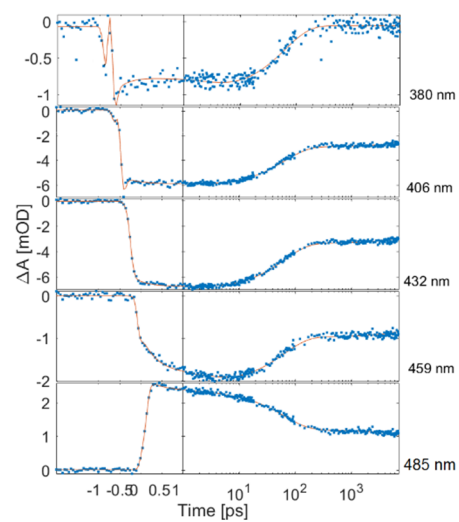
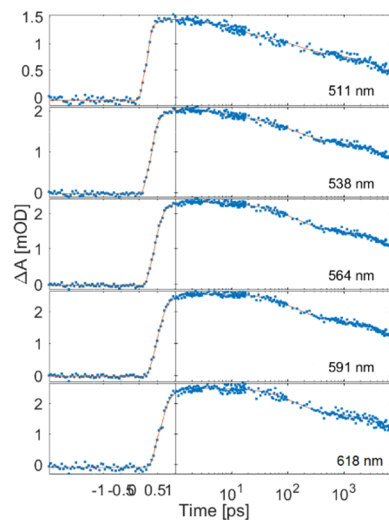
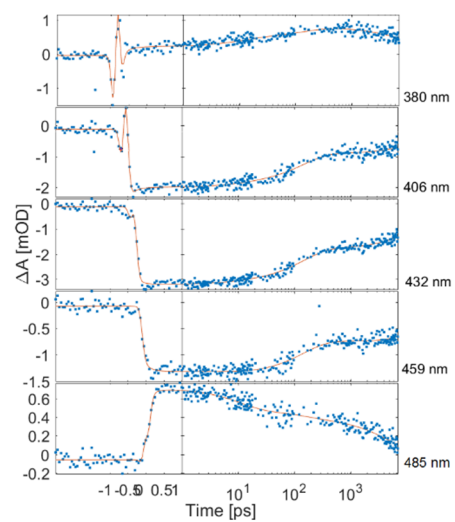
**(b)**



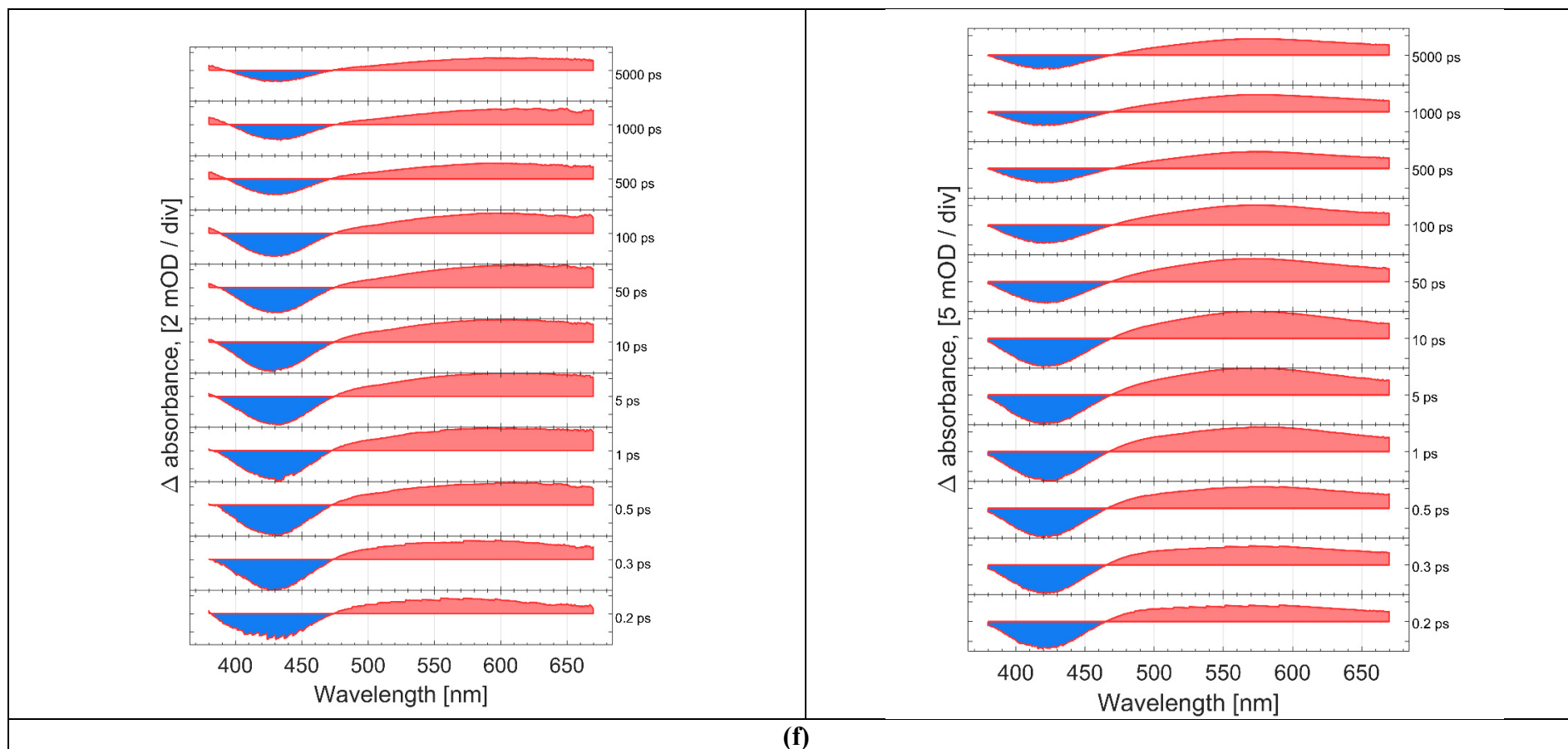
(c)



(d)

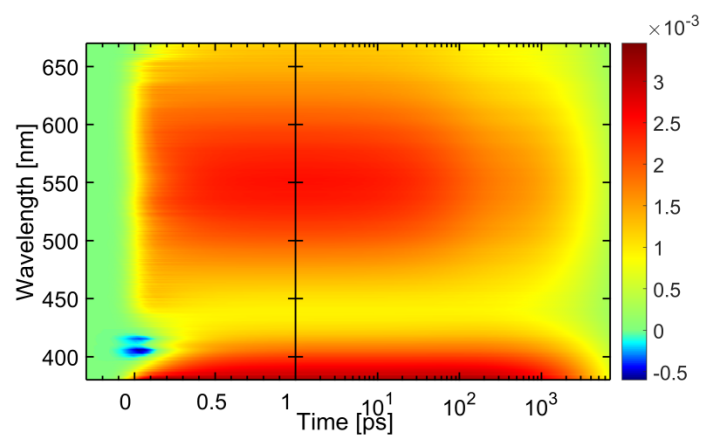


(e)

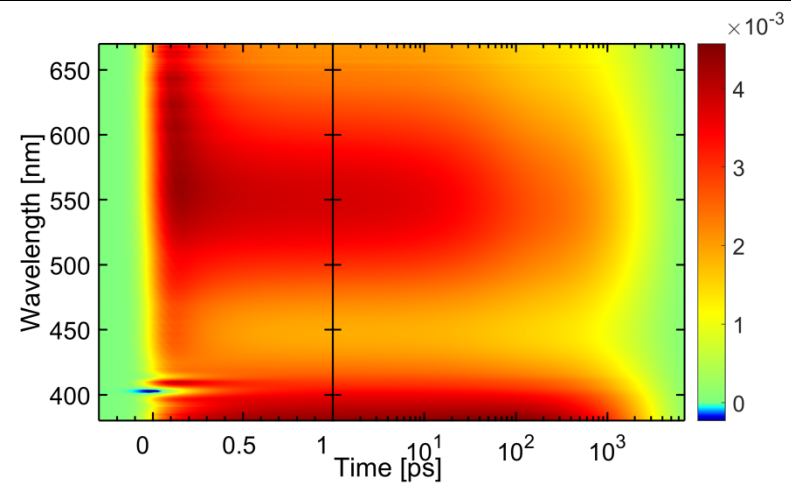


**Figure 37.** The fsTA 2D maps (a) and TA spectra at selected time delays (b and f)) decay associated spectra (DAS<sub>i</sub>) (c), species associated spectra (SAS<sub>i</sub>) (d) and time traces at several wavelength (e) for **4** in chloroform and acetonitrile.

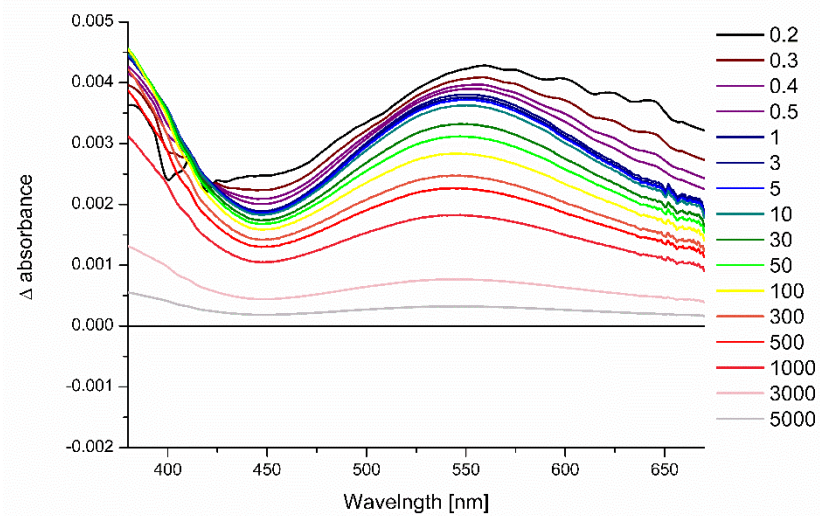
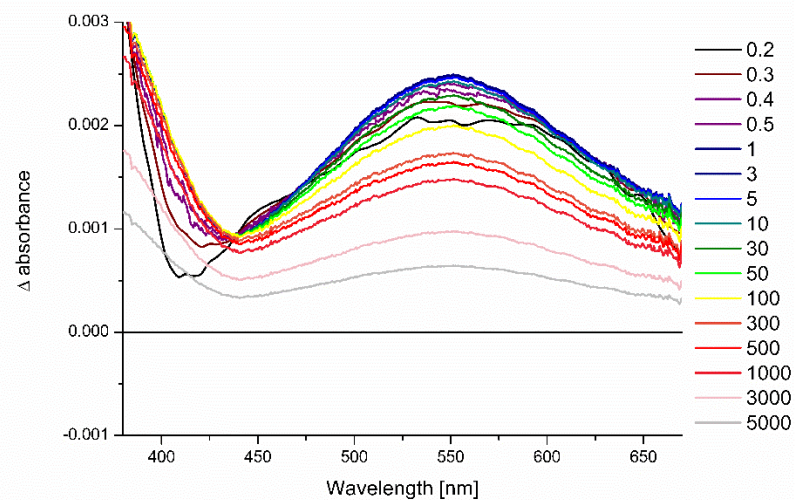
**3 in CHCl<sub>3</sub>**



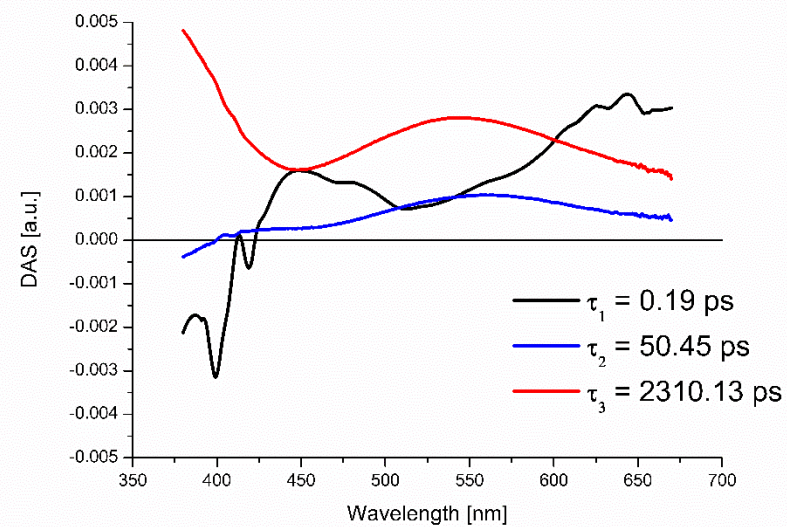
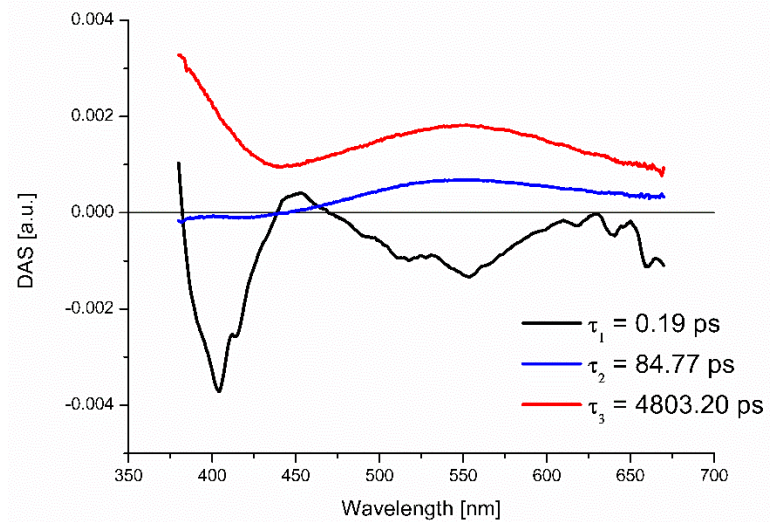
**3 in CH<sub>3</sub>CN**



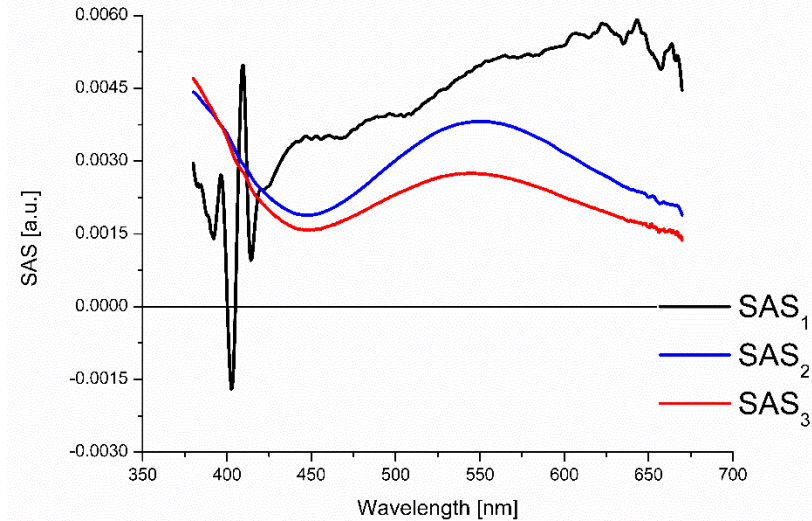
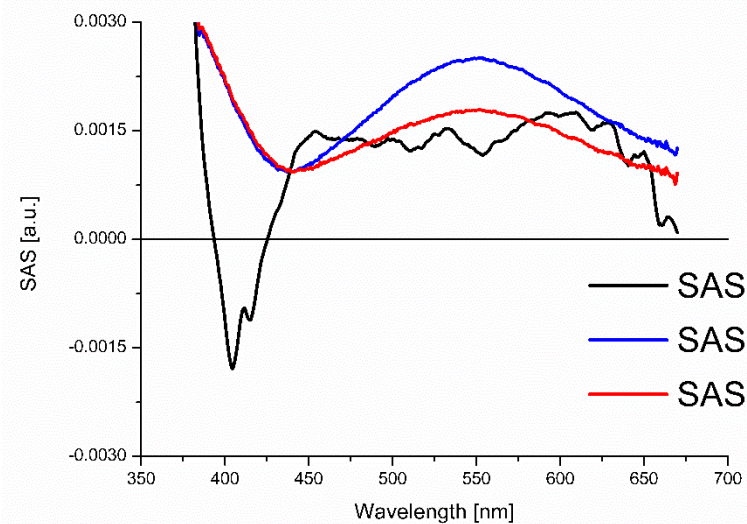
**(a)**



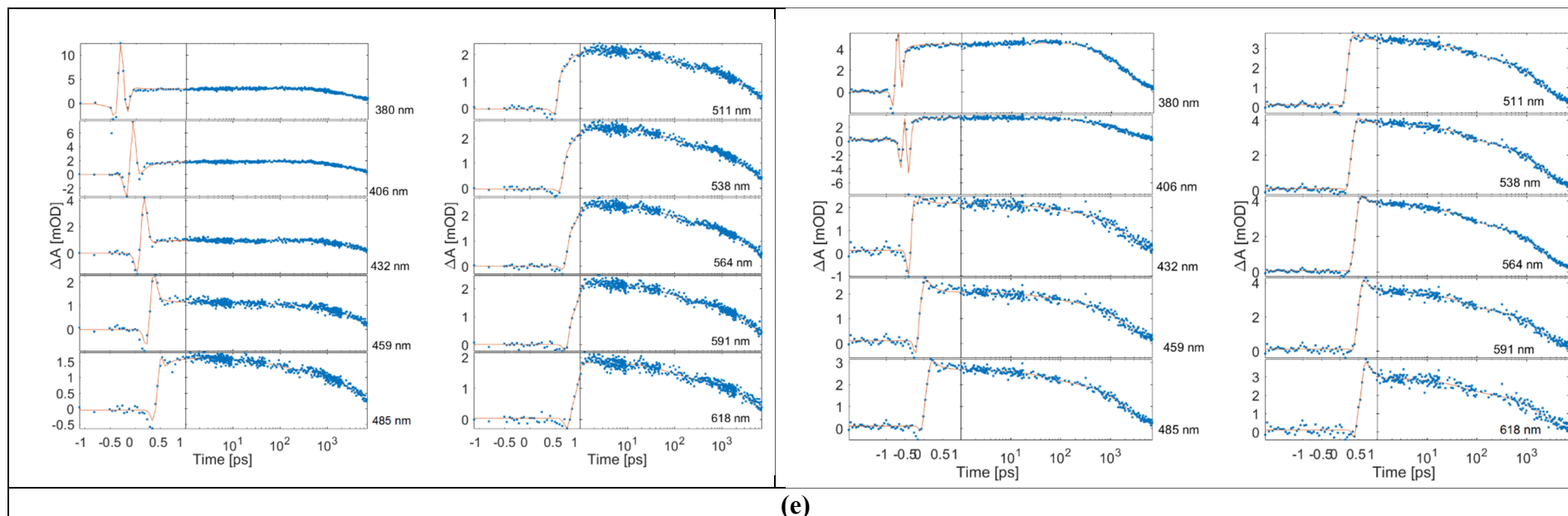
**(b)**

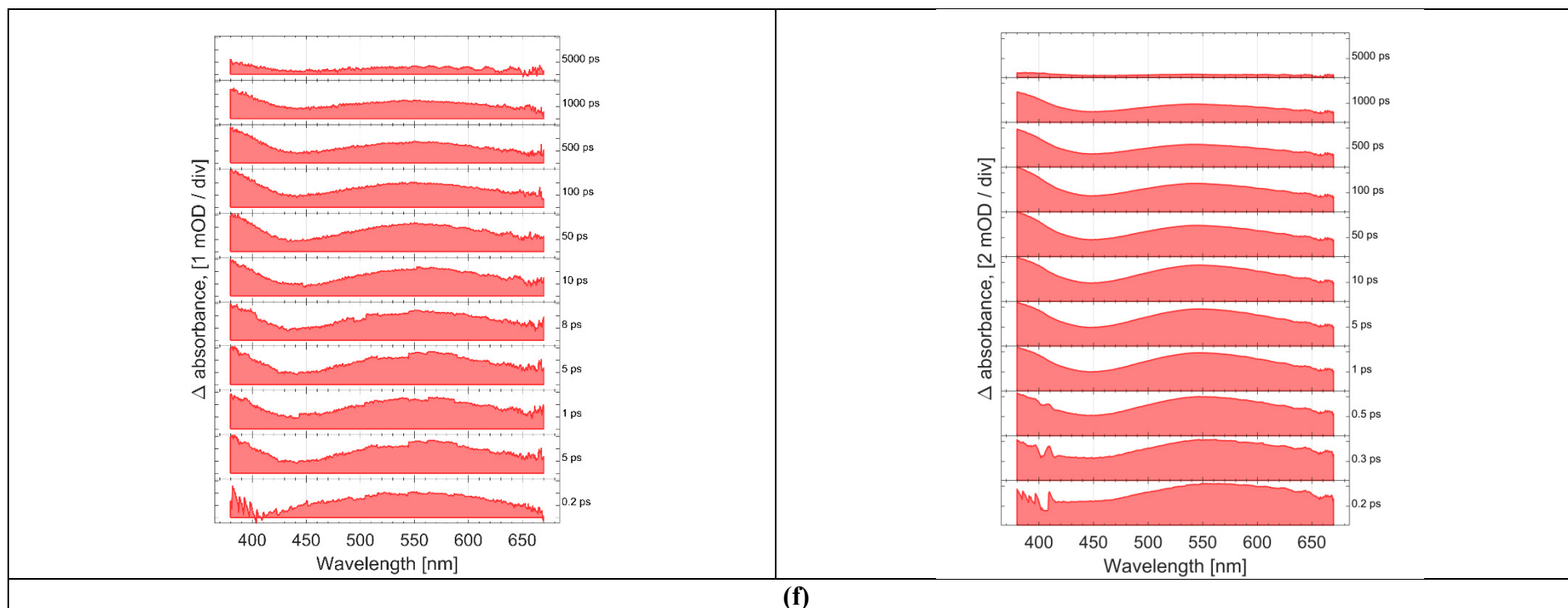


(c)



(d)





**Figure 38.** The fsTA 2D maps (a) and TA spectra at selected time delays (b and f)) decay associated spectra (DAS<sub>i</sub>) (c), species associated spectra (SAS<sub>i</sub>) (d) and time traces at several wavelength (e) for **3** in chloroform and acetonitrile.