

# **Synthesis, Structure and Photophysical Properties of Highly Luminescent Terpyridine–Diphenylacetylene Hybrid Fluorophore and its Metal Complexes**

Biswa Nath Ghosh,<sup>a,b</sup> Filip Topić,<sup>a</sup> Prasit Kumar Sahoo,<sup>c</sup> Prasenjit Mal,<sup>\*,c</sup> Jarno Linnera,<sup>a</sup> Elina Kalenius,<sup>a</sup> Heikki M. Tuononen<sup>\*,a</sup> and Kari Rissanen<sup>\*,a</sup>

<sup>a</sup>Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014 Jyväskylä, Finland.

<sup>b</sup>Department of Chemistry, Veer Surendra Sai University of Technology, Burla, Sambalpur-768018, Odisha, India

<sup>c</sup>School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar; Institute of Physics Campus, P.O. Sainik School; Bhubaneswar, Odisha 751005, India.

\* Corresponding authors:

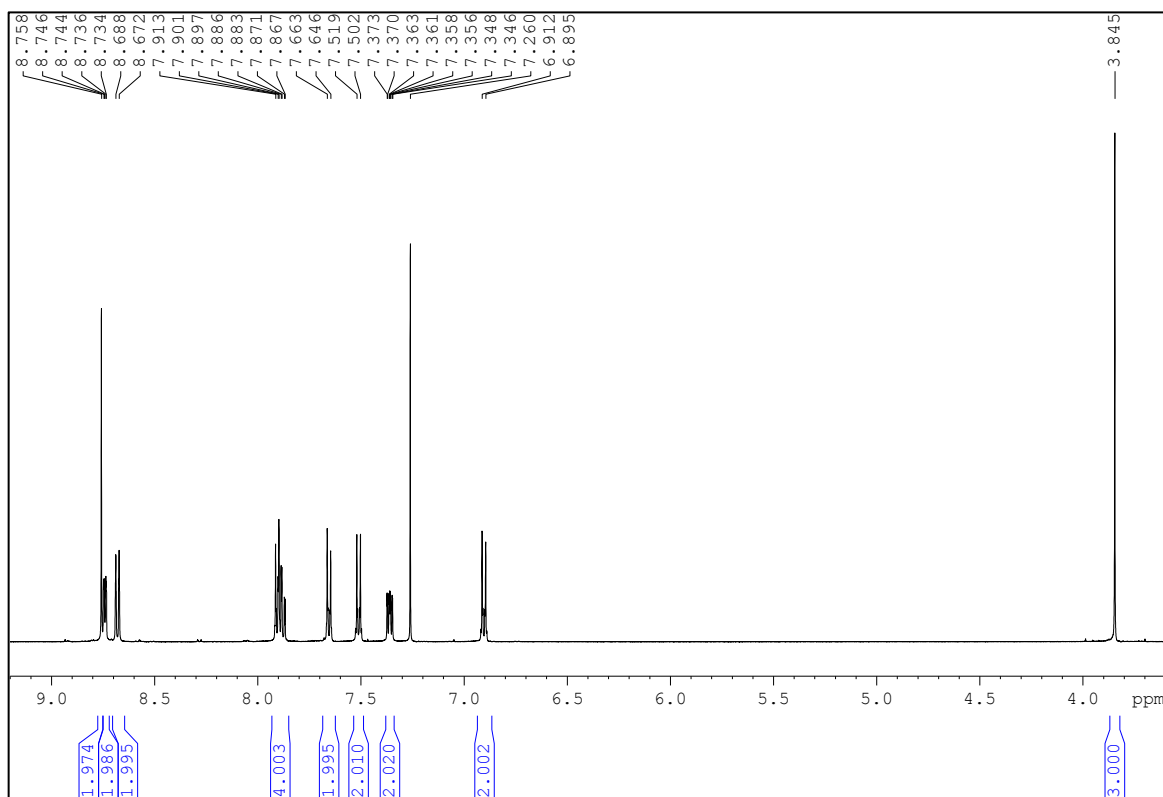
Prasenjit Mal, Tel.: +91 674 2304073, E-mail: [pmal@niser.ac.in](mailto:pmal@niser.ac.in),  
<http://www.niser.ac.in/~pmal/>

Heikki M. Tuononen, Tel.: +358 45 235 8588, E-mail: [heikki.m.tuononen@jyu.fi](mailto:heikki.m.tuononen@jyu.fi),  
<https://www.jyu.fi/kemia/en/research/main-group-chemistry>

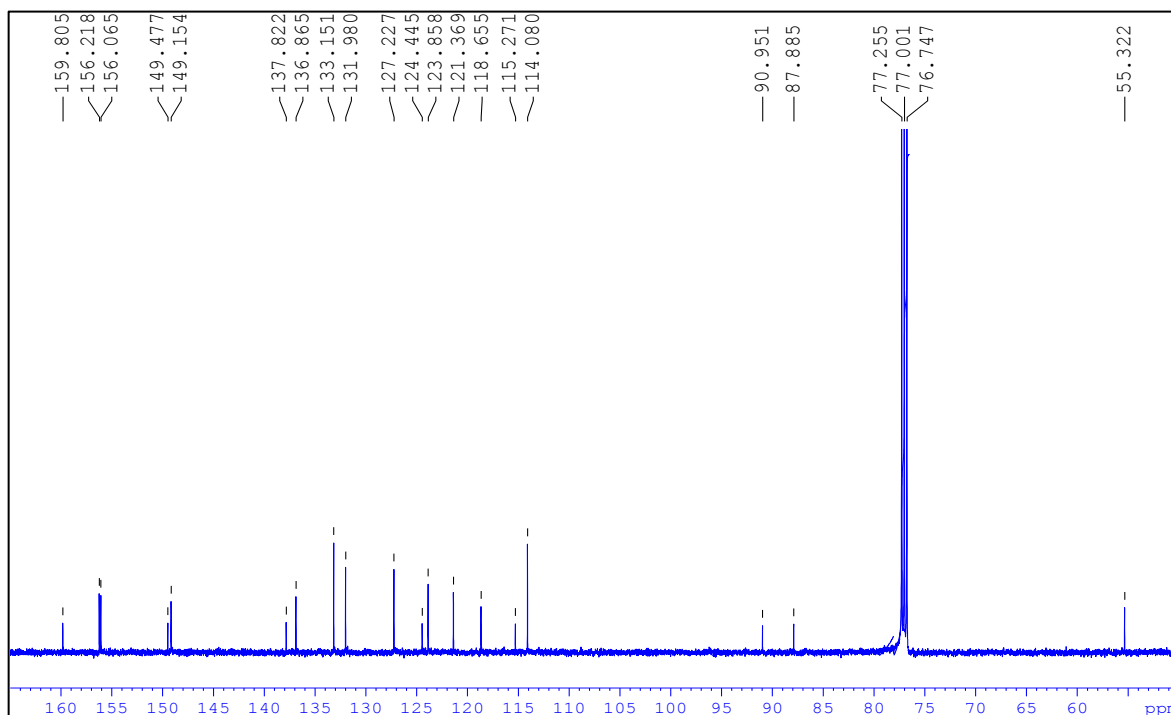
Kari Rissanen, Tel.: +358 50 562 3721, E-mail: [kari.t.rissanen@jyu.fi](mailto:kari.t.rissanen@jyu.fi),  
<https://www.jyu.fi/kemia/tutkimus/orgaaninen/staff/rissanen>

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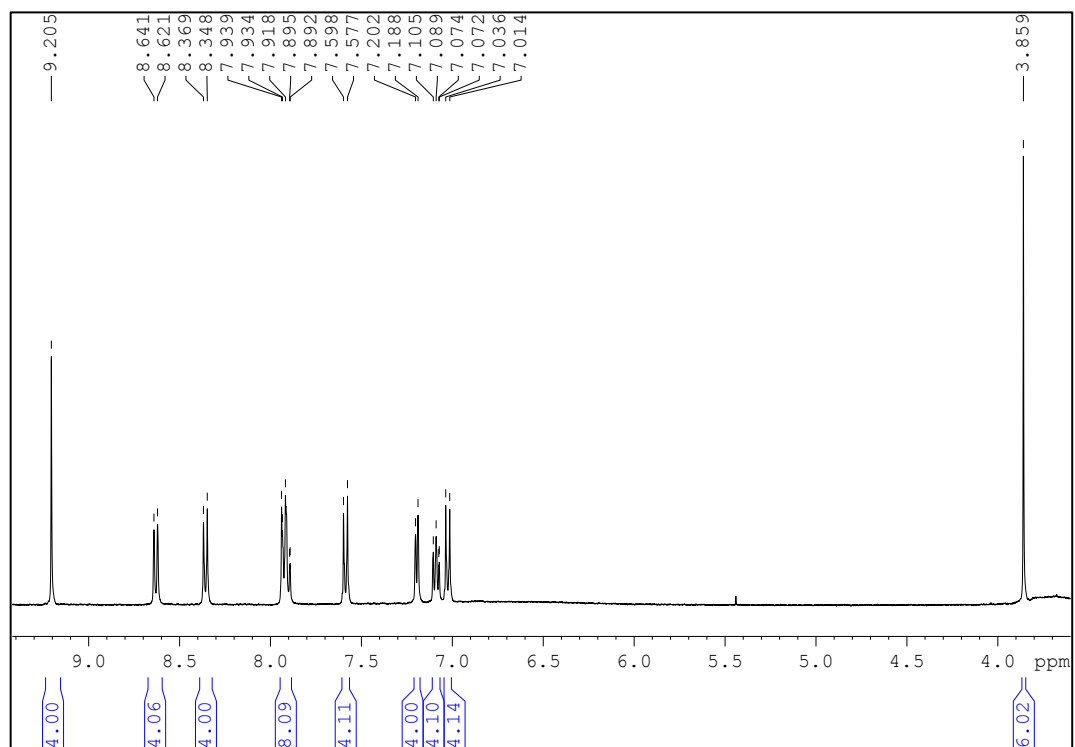
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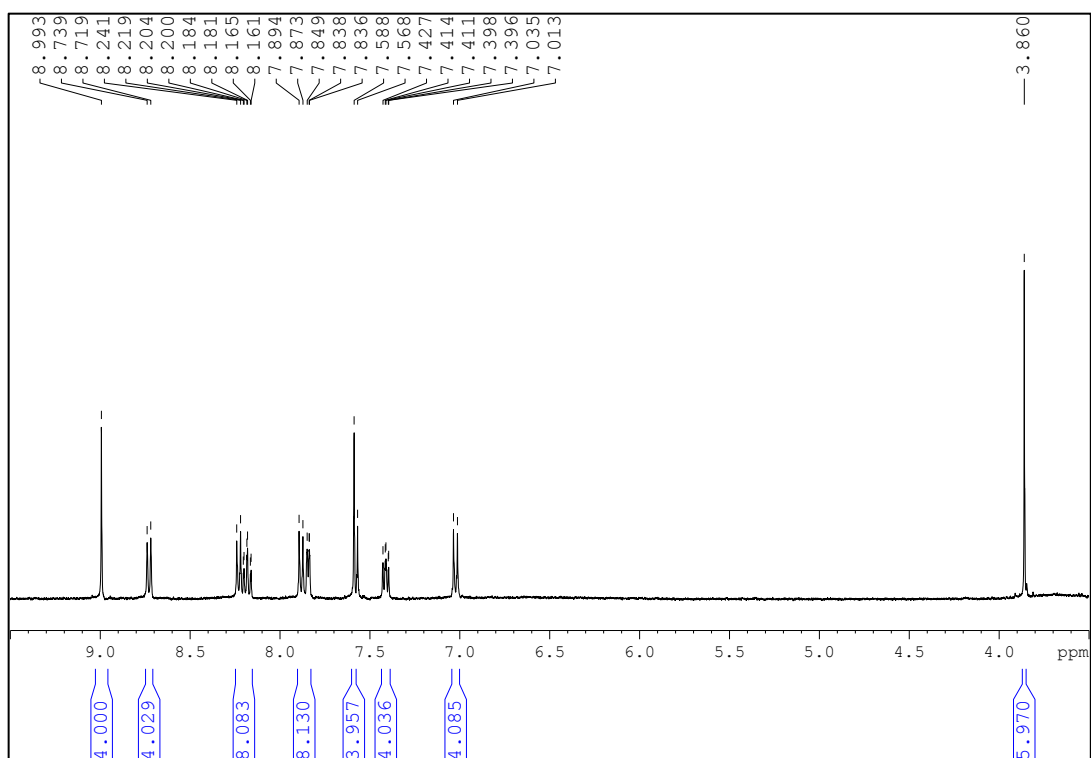
**Fig. S1** <sup>1</sup>H NMR spectrum of **L** in CDCl<sub>3</sub> at 27 °C.



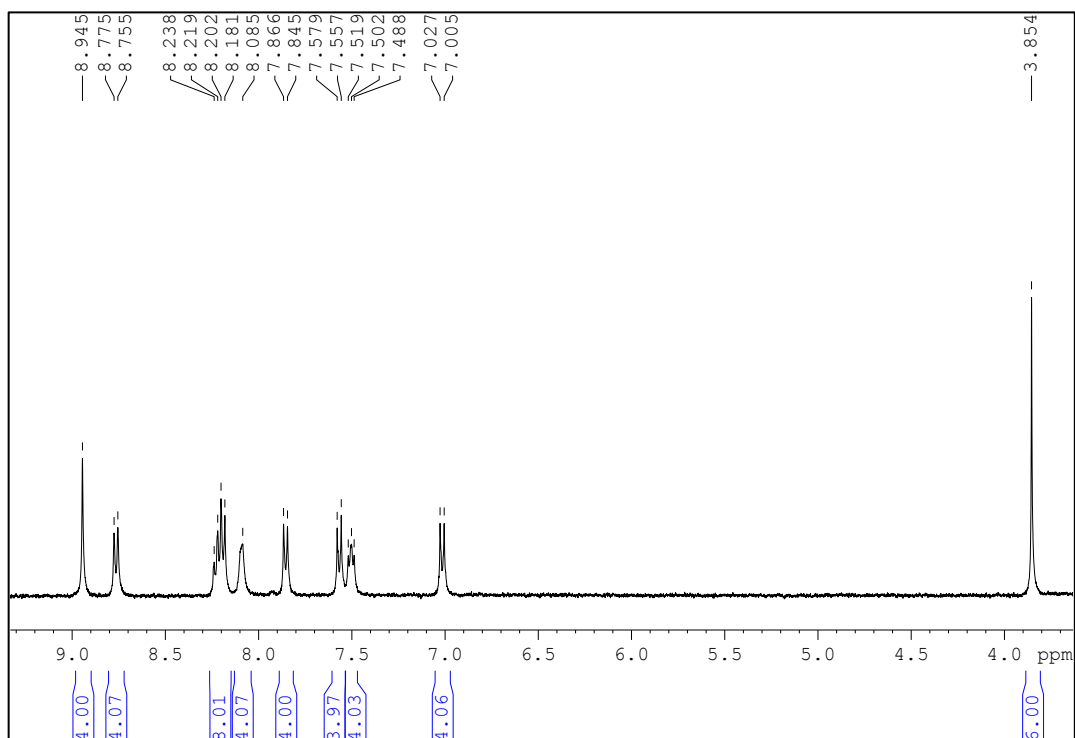
**Fig. S2** <sup>13</sup>C NMR spectrum of **L** in CDCl<sub>3</sub> 27 °C.



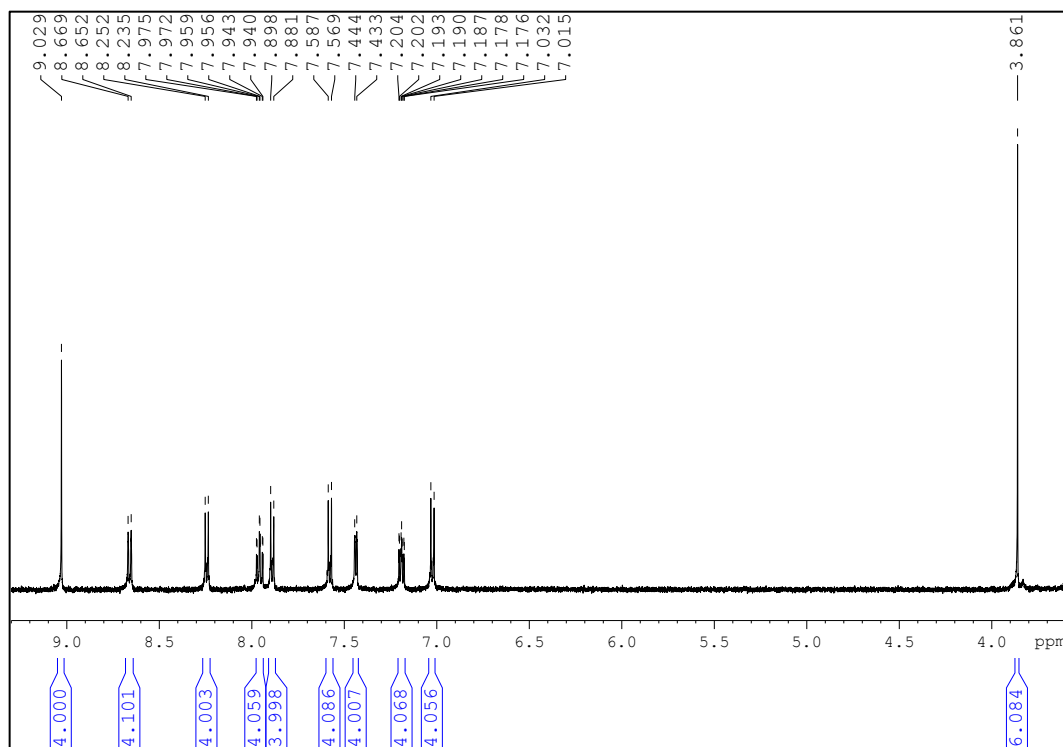
**Fig. S3** <sup>1</sup>H NMR spectrum of complex **1** in CD<sub>3</sub>CN at 27 °C.



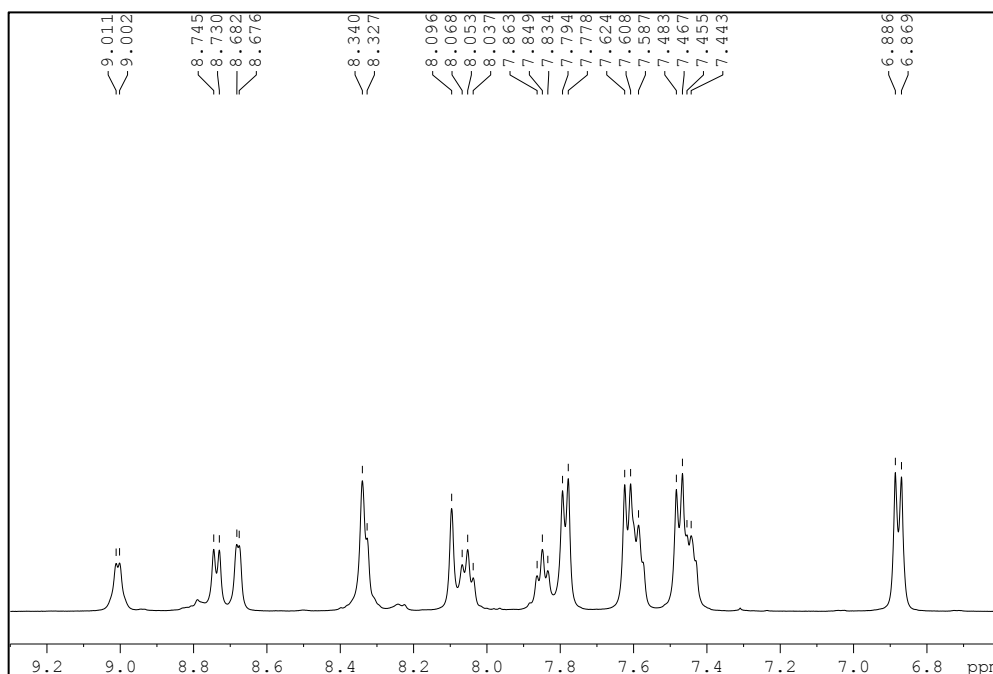
**Fig. S4** <sup>1</sup>H NMR spectrum of complex **2** in CD<sub>3</sub>CN at 27 °C.



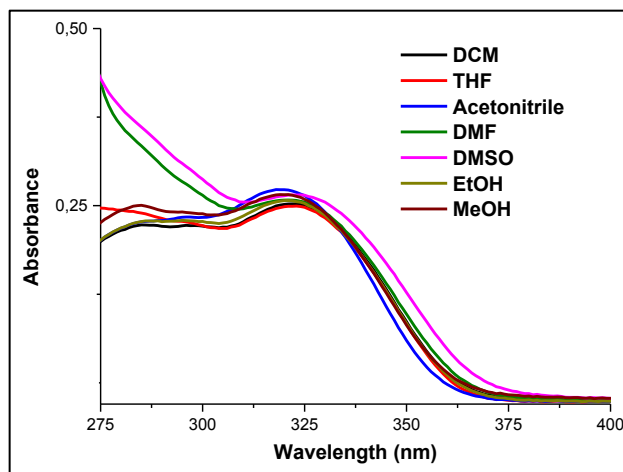
**Fig. S5** <sup>1</sup>H NMR spectrum of complex **3** in CD<sub>3</sub>CN at 27 °C.



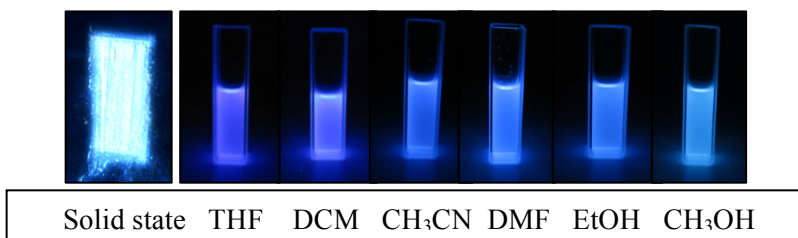
**Fig. S6** <sup>1</sup>H NMR spectrum of complex **4** in CD<sub>3</sub>CN at 27 °C.



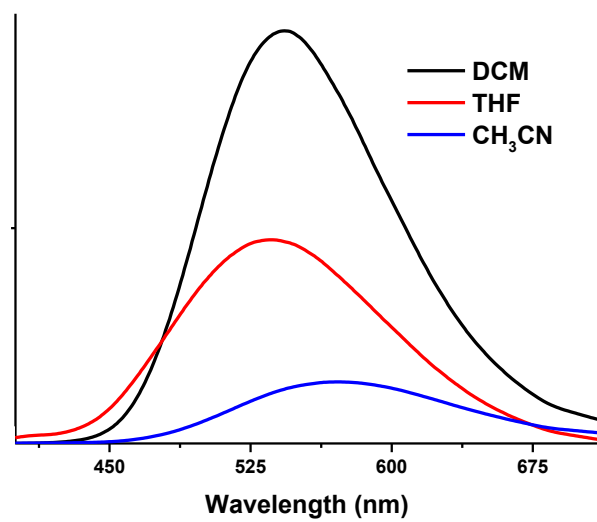
**Fig. S7** Aromatic region in the  $^1\text{H}$  NMR spectrum of complex **5** in  $\text{CD}_2\text{Cl}_2$  at  $-60\text{ }^\circ\text{C}$ .



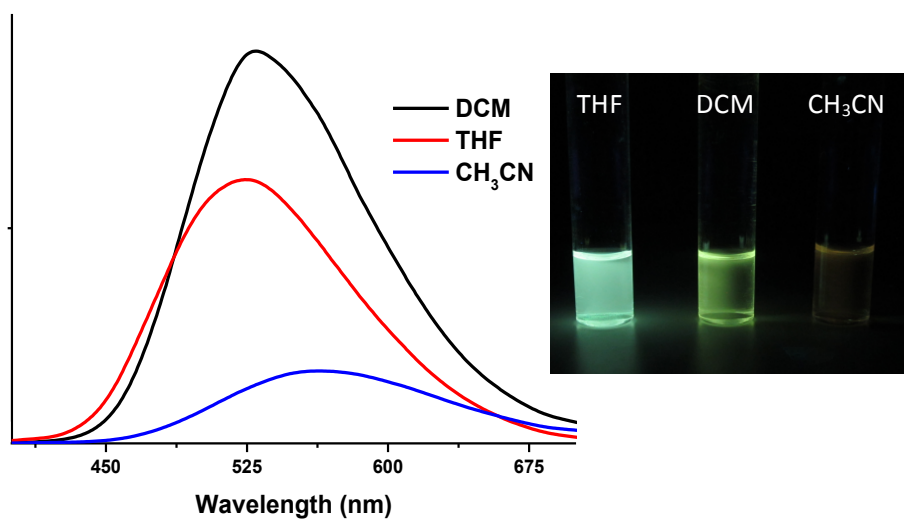
**Fig. S8** UV-Vis spectra of mono-terpyridine ligand **L** in different solvents.



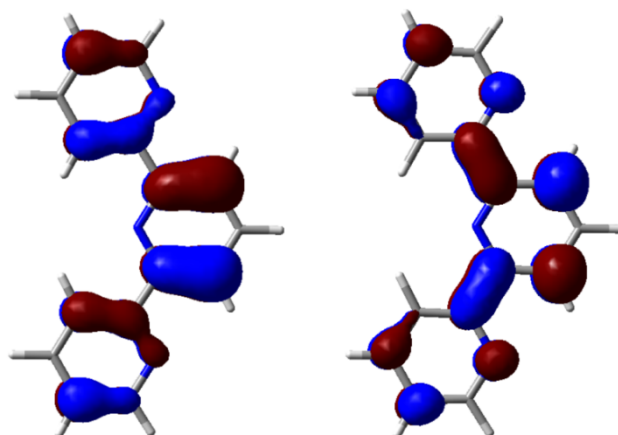
**Fig. S9** Fluorescence of **L** in solid state and in different solvents under UV lamp (365 nm).



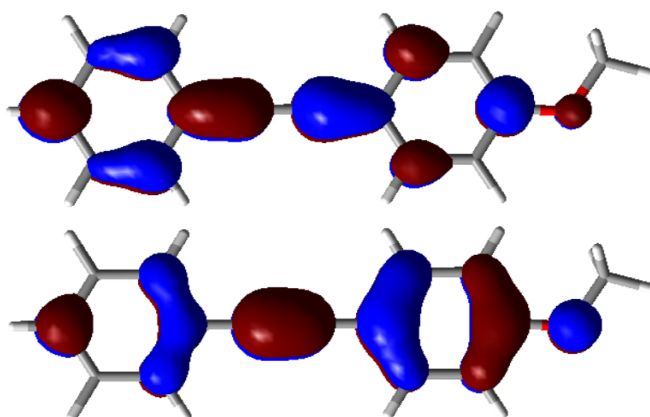
**Fig. S10** Emission spectra of complex **2** in different solvents.



**Fig. S11** Emission spectra of complex **3** in different solvents.



**Fig. S12** HOMO (left) and LUMO (right) of parent terpyridine ligand.



**Fig. S13** HOMO (bottom) and LUMO (top) of methoxy substituted 1,2-diphenylacetylene.

**Table S1** Selected optimized (PBE1PBE/def-TZVP) bond lengths (Å) and angles (°) for **L**

| <b>Ligand L</b> |       |             |       |             |       |
|-----------------|-------|-------------|-------|-------------|-------|
| C2-N1           | 1.326 | C7-N8       | 1.332 | C13-N18     | 1.335 |
| C6-N1           | 1.335 | C9-N8       | 1.332 | C17-N18     | 1.326 |
| C6-C7           | 1.485 | C9-C13      | 1.485 | C11-C19     | 1.474 |
| C22-C25         | 1.417 | C25-C26     | 1.210 | C26-C27     | 1.417 |
| C2-C3           | 1.388 | C4-C5       | 1.383 | C7-C12      | 1.391 |
| C3-C4           | 1.387 | C5-C6       | 1.395 | C9-C10      | 1.391 |
| C10-C11         | 1.392 | C30-O33     | 1.352 | C34-O33     | 1.410 |
| N1-C2-C3        | 123.6 | N1-C6-C5    | 122.3 | N1-C6-C7    | 116.9 |
| N8-C7-C12       | 122.7 | N8-C7-C6    | 117.1 | N8-C9-C10   | 122.7 |
| N8-C9-C13       | 117.1 | N18-C13-C14 | 122.3 | N18-C13-C9  | 116.9 |
| N18-C17-C16     | 123.6 | C2-N1-C6    | 118.3 | C7-N8-C9    | 118.3 |
| C17-N18-C13     | 118.3 | C30-O33-C34 | 118.1 | O33-C30-C31 | 124.5 |
| O33-C30-C29     | 115.9 | C26-C25-C22 | 179.9 | C25-C26-C27 | 179.9 |



Ground state geometry for L (gas phase)

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|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 4.071681  | -1.123361 | -0.053909 |
| C | 2.682003  | -1.184321 | -0.051356 |
| C | 1.945765  | -0.003815 | 0.005279  |
| C | 2.656443  | 1.192646  | 0.052654  |
| C | 4.047121  | 1.162041  | 0.038085  |
| N | 4.742271  | 0.026846  | -0.012070 |
| H | 2.207830  | -2.154578 | -0.114933 |
| H | 2.162061  | 2.152361  | 0.122320  |
| C | 4.821274  | 2.428734  | 0.090294  |
| C | 6.214887  | 2.411276  | 0.137109  |
| N | 4.121348  | 3.565811  | 0.091211  |
| C | 6.895190  | 3.614758  | 0.184145  |
| H | 6.728983  | 1.459677  | 0.135647  |
| C | 4.786137  | 4.712654  | 0.137763  |
| C | 6.170494  | 4.797276  | 0.184939  |
| H | 7.979096  | 3.630726  | 0.221273  |
| H | 4.179887  | 5.614697  | 0.136984  |
| H | 6.660481  | 5.762925  | 0.221564  |
| C | 4.872553  | -2.372906 | -0.115139 |
| C | 6.264832  | -2.325368 | -0.176833 |
| N | 4.197434  | -3.524864 | -0.108871 |
| C | 6.970498  | -3.513861 | -0.231389 |
| H | 6.758315  | -1.362922 | -0.180605 |
| C | 4.886283  | -4.657066 | -0.162811 |
| C | 6.271626  | -4.711778 | -0.224734 |
| H | 8.054041  | -3.506329 | -0.279979 |
| H | 4.299665  | -5.571966 | -0.155761 |
| H | 6.781932  | -5.666624 | -0.266735 |
| C | 0.471484  | -0.020550 | 0.015210  |
| C | -0.262778 | 1.001262  | -0.591621 |
| C | -0.230126 | -1.059330 | 0.631916  |
| C | -1.644001 | 0.987417  | -0.587169 |
| H | 0.257784  | 1.807793  | -1.095656 |
| C | -1.611123 | -1.078456 | 0.645899  |
| H | 0.316241  | -1.853220 | 1.128683  |
| C | -2.345163 | -0.054158 | 0.033985  |
| H | -2.198270 | 1.782256  | -1.072062 |
| H | -2.139817 | -1.886286 | 1.137814  |
| C | -3.761887 | -0.072425 | 0.043039  |
| C | -4.971568 | -0.089851 | 0.050882  |
| C | -6.388242 | -0.117008 | 0.062914  |
| C | -7.133579 | 0.913729  | -0.513585 |

|   |            |           |           |
|---|------------|-----------|-----------|
| C | -7.082506  | -1.183936 | 0.655851  |
| C | -8.519524  | 0.891934  | -0.505507 |
| H | -6.615289  | 1.745789  | -0.975532 |
| C | -8.458830  | -1.212904 | 0.667857  |
| H | -6.521231  | -1.992941 | 1.108202  |
| C | -9.190985  | -0.175238 | 0.087023  |
| H | -9.063111  | 1.708749  | -0.962046 |
| H | -8.997746  | -2.034834 | 1.124034  |
| O | -10.536009 | -0.294289 | 0.148412  |
| C | -11.320757 | 0.725852  | -0.427076 |
| H | -12.357328 | 0.434274  | -0.267997 |
| H | -11.141444 | 1.692574  | 0.055953  |
| H | -11.134596 | 0.818181  | -1.502637 |

Ground state geometry for L  
(CH<sub>3</sub>CN)

55

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -4.068291 | -1.124875 | 0.054265  |
| C | -2.678245 | -1.185531 | 0.048653  |
| C | -1.941916 | -0.004508 | -0.006330 |
| C | -2.651368 | 1.193268  | -0.050819 |
| C | -4.042486 | 1.164604  | -0.036889 |
| N | -4.736005 | 0.027719  | 0.013306  |
| H | -2.198909 | -2.153337 | 0.106867  |
| H | -2.150619 | 2.149710  | -0.116123 |
| C | -4.822283 | 2.429219  | -0.088917 |
| C | -6.215719 | 2.406507  | -0.130017 |
| N | -4.126770 | 3.570767  | -0.094970 |
| C | -6.902685 | 3.607649  | -0.176301 |
| H | -6.732239 | 1.456154  | -0.124659 |
| C | -4.798057 | 4.716259  | -0.140590 |
| C | -6.183371 | 4.793339  | -0.182030 |
| H | -7.986405 | 3.617928  | -0.208676 |
| H | -4.198667 | 5.622424  | -0.143714 |
| H | -6.677581 | 5.756501  | -0.217930 |
| C | -4.876080 | -2.371294 | 0.116600  |
| C | -6.268645 | -2.317317 | 0.156101  |
| N | -4.206156 | -3.527962 | 0.132382  |
| C | -6.982247 | -3.502438 | 0.211852  |
| H | -6.763818 | -1.355748 | 0.142091  |
| C | -4.902801 | -4.657811 | 0.186829  |
| C | -6.289553 | -4.703756 | 0.227924  |
| H | -8.065955 | -3.488281 | 0.243069  |
| H | -4.323723 | -5.577030 | 0.197834  |
| H | -6.805049 | -5.655381 | 0.271393  |
| C | -0.467015 | -0.022073 | -0.017674 |
| C | 0.267854  | 0.998987  | 0.591240  |
| C | 0.232618  | -1.061041 | -0.637805 |
| C | 1.649716  | 0.984354  | 0.585639  |
| H | -0.248232 | 1.806808  | 1.097469  |
| C | 1.614236  | -1.081548 | -0.653044 |
| H | -0.311592 | -1.855351 | -1.135908 |
| C | 2.348590  | -0.057814 | -0.038843 |
| H | 2.202109  | 1.779390  | 1.072476  |
| H | 2.138891  | -1.890339 | -1.147841 |
| C | 3.766402  | -0.076989 | -0.048579 |
| C | 4.977074  | -0.094747 | -0.056273 |
| C | 6.394593  | -0.120891 | -0.067032 |
| C | 7.137761  | 0.910829  | 0.514392  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 7.089493  | -1.186716 | -0.662739 |
| C | 8.523439  | 0.890887  | 0.508491  |
| H | 6.620893  | 1.742589  | 0.978814  |
| C | 8.466575  | -1.213250 | -0.672168 |
| H | 6.532765  | -1.996764 | -1.119246 |
| C | 9.197447  | -0.175174 | -0.086513 |
| H | 9.065087  | 1.706971  | 0.968054  |
| H | 9.002872  | -2.035679 | -1.131167 |
| O | 10.540278 | -0.290568 | -0.144617 |
| C | 11.327525 | 0.734728  | 0.437854  |
| H | 12.363471 | 0.441940  | 0.281618  |
| H | 11.147146 | 1.698482  | -0.047119 |
| H | 11.134489 | 0.822755  | 1.510947  |

# Ground state geometry for L (CH<sub>2</sub>Cl<sub>2</sub>)

55

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -4.069019 | -1.124540 | 0.054320  |
| C | -2.679063 | -1.185484 | 0.048825  |
| C | -1.942533 | -0.004733 | -0.007004 |
| C | -2.651994 | 1.192919  | -0.052076 |
| C | -4.043020 | 1.164268  | -0.037361 |
| N | -4.737045 | 0.027794  | 0.013303  |
| H | -2.200701 | -2.153718 | 0.108126  |
| H | -2.152040 | 2.149697  | -0.118679 |
| C | -4.821589 | 2.429451  | -0.089157 |
| C | -6.215071 | 2.407856  | -0.130408 |
| N | -4.125169 | 3.570191  | -0.094819 |
| C | -6.900878 | 3.609432  | -0.176821 |
| H | -6.731214 | 1.457324  | -0.125075 |
| C | -4.795319 | 4.715997  | -0.140560 |
| C | -6.180486 | 4.794493  | -0.182423 |
| H | -7.984647 | 3.620782  | -0.209442 |
| H | -4.194730 | 5.621432  | -0.143511 |
| H | -6.673843 | 5.758142  | -0.218536 |
| C | -4.875810 | -2.371383 | 0.116921  |
| C | -6.268241 | -2.318084 | 0.162511  |
| N | -4.205337 | -3.527537 | 0.127076  |
| C | -6.980912 | -3.503515 | 0.218720  |
| H | -6.762757 | -1.356153 | 0.152734  |
| C | -4.901042 | -4.657587 | 0.182086  |
| C | -6.287526 | -4.704522 | 0.229214  |
| H | -8.064547 | -3.490070 | 0.254771  |
| H | -4.321038 | -5.576322 | 0.188509  |
| H | -6.802365 | -5.656548 | 0.272948  |
| C | -0.467750 | -0.022373 | -0.018490 |
| C | 0.267223  | 0.998756  | 0.589914  |
| C | 0.231929  | -1.061426 | -0.638171 |
| C | 1.648981  | 0.984081  | 0.584252  |
| H | -0.249427 | 1.806460  | 1.095827  |
| C | 1.613456  | -1.081848 | -0.653503 |
| H | -0.312842 | -1.855673 | -1.135835 |
| C | 2.347974  | -0.058082 | -0.039824 |
| H | 2.201821  | 1.779052  | 1.070675  |
| H | 2.138558  | -1.890585 | -1.147896 |
| C | 3.765657  | -0.077217 | -0.049625 |
| C | 4.976198  | -0.094887 | -0.057271 |
| C | 6.393636  | -0.120701 | -0.067714 |
| C | 7.136391  | 0.909020  | 0.517111  |
| C | 7.089182  | -1.184268 | -0.666446 |
| C | 8.522116  | 0.889287  | 0.511704  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 6.618680  | 1.738938  | 0.983847  |
| C | 8.466173  | -1.210654 | -0.675505 |
| H | 6.532344  | -1.992712 | -1.125593 |
| C | 9.196535  | -0.174535 | -0.086325 |
| H | 9.063537  | 1.703945  | 0.974103  |
| H | 9.003444  | -2.031142 | -1.136726 |
| O | 10.539758 | -0.289739 | -0.144287 |
| C | 11.325808 | 0.732786  | 0.442005  |
| H | 12.362073 | 0.441163  | 0.285173  |
| H | 11.145729 | 1.698799  | -0.039060 |
| H | 11.132711 | 0.816921  | 1.515628  |

Excited state geometry for L (gas phase)

55

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 4.073659  | -1.120718 | -0.022371 |
| C | 2.692178  | -1.192581 | -0.012653 |
| C | 1.923371  | -0.010639 | 0.008583  |
| C | 2.652085  | 1.196500  | 0.022058  |
| C | 4.035260  | 1.171209  | 0.016552  |
| N | 4.755061  | 0.037044  | -0.006866 |
| H | 2.248225  | -2.177405 | -0.048500 |
| H | 2.175411  | 2.165704  | 0.063082  |
| C | 4.792094  | 2.443416  | 0.040321  |
| C | 6.189733  | 2.434148  | 0.041690  |
| N | 4.091080  | 3.583457  | 0.059270  |
| C | 6.867251  | 3.639343  | 0.063471  |
| H | 6.702540  | 1.482073  | 0.025995  |
| C | 4.754920  | 4.730078  | 0.080631  |
| C | 6.141157  | 4.821355  | 0.083579  |
| H | 7.952125  | 3.657644  | 0.064952  |
| H | 4.146930  | 5.631561  | 0.096014  |
| H | 6.628767  | 5.788827  | 0.101324  |
| C | 4.872546  | -2.366777 | -0.054935 |
| C | 6.268895  | -2.310789 | -0.072500 |
| N | 4.209983  | -3.529665 | -0.066059 |
| C | 6.986160  | -3.492613 | -0.102502 |
| H | 6.749818  | -1.342146 | -0.062497 |
| C | 4.911498  | -4.653431 | -0.095440 |
| C | 6.299964  | -4.698287 | -0.114548 |
| H | 8.070945  | -3.474460 | -0.116572 |
| H | 4.333812  | -5.574704 | -0.103992 |
| H | 6.819436  | -5.648901 | -0.138261 |
| C | 0.478971  | -0.034834 | 0.015503  |
| C | -0.286482 | 1.139717  | -0.224592 |
| C | -0.244384 | -1.234371 | 0.262199  |
| C | -1.652902 | 1.121908  | -0.221899 |
| H | 0.221546  | 2.071375  | -0.436754 |
| C | -1.610614 | -1.263054 | 0.270443  |
| H | 0.296487  | -2.148246 | 0.470216  |
| C | -2.365546 | -0.083036 | 0.026982  |
| H | -2.211562 | 2.030175  | -0.416925 |
| H | -2.136564 | -2.189686 | 0.469880  |
| C | -3.750791 | -0.106229 | 0.031310  |
| C | -4.980999 | -0.125740 | 0.034172  |
| C | -6.365951 | -0.147967 | 0.034760  |
| C | -7.116011 | 1.026838  | -0.226714 |

|   |            |           |           |
|---|------------|-----------|-----------|
| C | -7.081603  | -1.348800 | 0.296177  |
| C | -8.490754  | 1.009771  | -0.229143 |
| H | -6.585744  | 1.949793  | -0.427427 |
| C | -8.448621  | -1.364605 | 0.292703  |
| H | -6.524622  | -2.255426 | 0.498381  |
| C | -9.173846  | -0.187958 | 0.030259  |
| H | -9.032828  | 1.923906  | -0.432557 |
| H | -9.001772  | -2.275064 | 0.490010  |
| O | -10.505520 | -0.311386 | 0.049568  |
| C | -11.306565 | 0.827893  | -0.205930 |
| H | -12.337134 | 0.486658  | -0.140219 |
| H | -11.133791 | 1.608342  | 0.541335  |
| H | -11.118791 | 1.226751  | -1.207423 |

Excited state geometry for L  
(CH<sub>3</sub>CN)

55

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 0.000000  | 0.000000  | 0.000000  |
| C | 0.000000  | 0.000000  | 1.382408  |
| C | 1.220678  | 0.000000  | 2.099407  |
| C | 2.387868  | 0.000170  | 1.298409  |
| C | 2.290781  | 0.000788  | -0.080594 |
| N | 1.120703  | 0.000134  | -0.741868 |
| H | -0.959667 | 0.007978  | 1.878425  |
| H | 3.379780  | -0.008258 | 1.726096  |
| C | 3.521417  | -0.006453 | -0.912046 |
| C | 3.435577  | -0.086413 | -2.303523 |
| N | 4.698877  | 0.064112  | -0.278736 |
| C | 4.601506  | -0.089975 | -3.050034 |
| H | 2.460569  | -0.144034 | -2.768216 |
| C | 5.809193  | 0.058375  | -1.007161 |
| C | 5.821254  | -0.016116 | -2.393889 |
| H | 4.558782  | -0.151284 | -4.131990 |
| H | 6.743464  | 0.117379  | -0.455010 |
| H | 6.759375  | -0.015757 | -2.935406 |
| C | -1.285884 | 0.005634  | -0.743089 |
| C | -1.297301 | 0.048593  | -2.138732 |
| N | -2.416641 | -0.030805 | -0.027206 |
| C | -2.512799 | 0.051514  | -2.801534 |
| H | -0.356704 | 0.078962  | -2.671949 |
| C | -3.575354 | -0.026629 | -0.675877 |
| C | -3.684190 | 0.013077  | -2.059879 |
| H | -2.545504 | 0.084298  | -3.885077 |
| H | -4.469071 | -0.057217 | -0.058168 |
| H | -4.658089 | 0.013710  | -2.534049 |
| C | 1.271413  | -0.000713 | 3.535368  |
| C | 2.507289  | 0.086637  | 4.244637  |
| C | 0.088380  | -0.088999 | 4.329331  |
| C | 2.562770  | 0.086942  | 5.606943  |
| H | 3.437389  | 0.164421  | 3.696924  |
| C | 0.128489  | -0.091405 | 5.692121  |
| H | -0.877732 | -0.166152 | 3.847987  |
| C | 1.371711  | -0.002973 | 6.391942  |
| H | 3.518568  | 0.159086  | 6.112999  |
| H | -0.789487 | -0.164561 | 6.263795  |
| C | 1.419372  | -0.005288 | 7.766481  |
| C | 1.460840  | -0.008166 | 9.000170  |
| C | 1.503041  | -0.013327 | 10.378018 |
| C | 2.741029  | 0.071805  | 11.074182 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 0.306486  | -0.104849 | 11.148296 |
| C | 2.786973  | 0.065381  | 12.445186 |
| H | 3.659238  | 0.142527  | 10.504031 |
| C | 0.355346  | -0.110563 | 12.512418 |
| H | -0.645194 | -0.170347 | 10.635494 |
| C | 1.593188  | -0.026491 | 13.183152 |
| H | 3.743416  | 0.131244  | 12.946399 |
| H | -0.548904 | -0.180290 | 13.105147 |
| O | 1.531753  | -0.041298 | 14.512157 |
| C | 2.736756  | 0.035997  | 15.267625 |
| H | 2.431965  | 0.006508  | 16.310325 |
| H | 3.386464  | -0.814877 | 15.050042 |
| H | 3.263181  | 0.971442  | 15.064598 |

# Excited state geometry for L (CH<sub>2</sub>Cl<sub>2</sub>)

55

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 0.000000  | 0.000000  | 0.000000  |
| C | 0.000000  | 0.000000  | 1.382408  |
| C | 1.220678  | 0.000000  | 2.099407  |
| C | 2.387868  | 0.000170  | 1.298409  |
| C | 2.290781  | 0.000788  | -0.080594 |
| N | 1.120703  | 0.000134  | -0.741868 |
| H | -0.959667 | 0.007978  | 1.878425  |
| H | 3.379780  | -0.008258 | 1.726096  |
| C | 3.521417  | -0.006453 | -0.912046 |
| C | 3.435577  | -0.086413 | -2.303523 |
| N | 4.698877  | 0.064112  | -0.278736 |
| C | 4.601506  | -0.089975 | -3.050034 |
| H | 2.460569  | -0.144034 | -2.768216 |
| C | 5.809193  | 0.058375  | -1.007161 |
| C | 5.821254  | -0.016116 | -2.393889 |
| H | 4.558782  | -0.151284 | -4.131990 |
| H | 6.743464  | 0.117379  | -0.455010 |
| H | 6.759375  | -0.015757 | -2.935406 |
| C | -1.285884 | 0.005634  | -0.743089 |
| C | -1.297301 | 0.048593  | -2.138732 |
| N | -2.416641 | -0.030805 | -0.027206 |
| C | -2.512799 | 0.051514  | -2.801534 |
| H | -0.356704 | 0.078962  | -2.671949 |
| C | -3.575354 | -0.026629 | -0.675877 |
| C | -3.684190 | 0.013077  | -2.059879 |
| H | -2.545504 | 0.084298  | -3.885077 |
| H | -4.469071 | -0.057217 | -0.058168 |
| H | -4.658089 | 0.013710  | -2.534049 |
| C | 1.271413  | -0.000713 | 3.535368  |
| C | 2.507289  | 0.086637  | 4.244637  |
| C | 0.088380  | -0.088999 | 4.329331  |
| C | 2.562770  | 0.086942  | 5.606943  |
| H | 3.437389  | 0.164421  | 3.696924  |
| C | 0.128489  | -0.091405 | 5.692121  |
| H | -0.877732 | -0.166152 | 3.847987  |
| C | 1.371711  | -0.002973 | 6.391942  |
| H | 3.518568  | 0.159086  | 6.112999  |
| H | -0.789487 | -0.164561 | 6.263795  |
| C | 1.419372  | -0.005288 | 7.766481  |
| C | 1.460840  | -0.008166 | 9.000170  |
| C | 1.503041  | -0.013327 | 10.378018 |
| C | 2.741029  | 0.071805  | 11.074182 |
| C | 0.306486  | -0.104849 | 11.148296 |
| C | 2.786973  | 0.065381  | 12.445186 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 3.659238  | 0.142527  | 10.504031 |
| C | 0.355346  | -0.110563 | 12.512418 |
| H | -0.645194 | -0.170347 | 10.635494 |
| C | 1.593188  | -0.026491 | 13.183152 |
| H | 3.743416  | 0.131244  | 12.946399 |
| H | -0.548904 | -0.180290 | 13.105147 |
| O | 1.531753  | -0.041298 | 14.512157 |
| C | 2.736756  | 0.035997  | 15.267625 |
| H | 2.431965  | 0.006508  | 16.310325 |
| H | 3.386464  | -0.814877 | 15.050042 |
| H | 3.263181  | 0.971442  | 15.064598 |

## Excitation energies and oscillator strengths for L (gas phase)

|               |           |           |           |           |          |              |
|---------------|-----------|-----------|-----------|-----------|----------|--------------|
| Excited State | 1:        | Singlet-A | 3.5746 eV | 346.85 nm | f=1.3193 | <S**2>=0.000 |
|               | 115 ->116 | 0.69654   |           |           |          |              |
| Excited State | 2:        | Singlet-A | 3.7969 eV | 326.54 nm | f=0.0021 | <S**2>=0.000 |
|               | 113 ->117 | 0.11798   |           |           |          |              |
|               | 114 ->116 | -0.18847  |           |           |          |              |
|               | 115 ->117 | 0.66690   |           |           |          |              |
| Excited State | 3:        | Singlet-A | 4.1398 eV | 299.49 nm | f=0.1688 | <S**2>=0.000 |
|               | 113 ->117 | -0.10518  |           |           |          |              |
|               | 114 ->116 | 0.64634   |           |           |          |              |
|               | 115 ->117 | 0.21230   |           |           |          |              |
| Excited State | 4:        | Singlet-A | 4.2778 eV | 289.83 nm | f=0.0029 | <S**2>=0.000 |
|               | 106 ->116 | 0.13890   |           |           |          |              |
|               | 110 ->117 | -0.17766  |           |           |          |              |
|               | 112 ->116 | 0.60714   |           |           |          |              |
|               | 112 ->118 | -0.24415  |           |           |          |              |
| Excited State | 5:        | Singlet-A | 4.2828 eV | 289.49 nm | f=0.5576 | <S**2>=0.000 |
|               | 114 ->117 | -0.20451  |           |           |          |              |
|               | 115 ->118 | 0.65880   |           |           |          |              |
| Excited State | 6:        | Singlet-A | 4.3648 eV | 284.06 nm | f=0.0029 | <S**2>=0.000 |
|               | 110 ->116 | -0.18733  |           |           |          |              |
|               | 110 ->118 | 0.17507   |           |           |          |              |
|               | 112 ->117 | 0.63014   |           |           |          |              |
| Excited State | 7:        | Singlet-A | 4.5224 eV | 274.16 nm | f=0.0539 | <S**2>=0.000 |
|               | 114 ->117 | 0.64494   |           |           |          |              |
|               | 114 ->120 | -0.11194  |           |           |          |              |
|               | 115 ->118 | 0.20725   |           |           |          |              |
| Excited State | 8:        | Singlet-A | 4.5754 eV | 270.98 nm | f=0.0011 | <S**2>=0.000 |
|               | 109 ->116 | 0.38220   |           |           |          |              |
|               | 110 ->117 | 0.21020   |           |           |          |              |
|               | 112 ->118 | 0.10108   |           |           |          |              |
|               | 113 ->122 | 0.10811   |           |           |          |              |
|               | 115 ->121 | 0.21043   |           |           |          |              |
|               | 115 ->122 | 0.43945   |           |           |          |              |
| Excited State | 9:        | Singlet-A | 4.6128 eV | 268.78 nm | f=0.0122 | <S**2>=0.000 |
|               | 108 ->116 | -0.18448  |           |           |          |              |
|               | 108 ->118 | -0.14461  |           |           |          |              |
|               | 108 ->123 | -0.10564  |           |           |          |              |
|               | 110 ->117 | -0.19664  |           |           |          |              |

|           |          |
|-----------|----------|
| 115 ->121 | 0.56700  |
| 115 ->122 | -0.12742 |

Excited State 10: Singlet-A 4.6244 eV 268.11 nm f=0.0031  $\langle S^2 \rangle = 0.000$

|           |          |
|-----------|----------|
| 106 ->116 | 0.21646  |
| 106 ->118 | -0.13811 |
| 109 ->116 | -0.17151 |
| 110 ->117 | 0.46010  |
| 111 ->117 | 0.14513  |
| 112 ->116 | 0.12568  |
| 112 ->119 | 0.15714  |
| 115 ->121 | 0.14647  |
| 115 ->122 | -0.25476 |



## Excitation energies and oscillator strengths for L (CH<sub>3</sub>CN)

|               |           |           |           |           |          |              |
|---------------|-----------|-----------|-----------|-----------|----------|--------------|
| Excited State | 1:        | Singlet-A | 3.4863 eV | 355.63 nm | f=1.4913 | <S**2>=0.000 |
|               | 115 ->116 | 0.69368   |           |           |          |              |
| Excited State | 2:        | Singlet-A | 3.8089 eV | 325.51 nm | f=0.0049 | <S**2>=0.000 |
|               | 113 ->117 | 0.12161   |           |           |          |              |
|               | 114 ->116 | 0.21303   |           |           |          |              |
|               | 115 ->117 | 0.65829   |           |           |          |              |
| Excited State | 3:        | Singlet-A | 4.0855 eV | 303.48 nm | f=0.2165 | <S**2>=0.000 |
|               | 114 ->116 | 0.64388   |           |           |          |              |
|               | 114 ->118 | 0.11218   |           |           |          |              |
|               | 115 ->117 | -0.23546  |           |           |          |              |
| Excited State | 4:        | Singlet-A | 4.2768 eV | 289.90 nm | f=0.5265 | <S**2>=0.000 |
|               | 114 ->117 | -0.19866  |           |           |          |              |
|               | 115 ->116 | 0.10080   |           |           |          |              |
|               | 115 ->118 | 0.65814   |           |           |          |              |
| Excited State | 5:        | Singlet-A | 4.2830 eV | 289.48 nm | f=0.0029 | <S**2>=0.000 |
|               | 106 ->116 | 0.15454   |           |           |          |              |
|               | 110 ->117 | 0.15988   |           |           |          |              |
|               | 112 ->116 | 0.61178   |           |           |          |              |
|               | 112 ->118 | 0.23956   |           |           |          |              |
| Excited State | 6:        | Singlet-A | 4.3902 eV | 282.41 nm | f=0.0008 | <S**2>=0.000 |
|               | 110 ->116 | 0.18974   |           |           |          |              |
|               | 110 ->118 | 0.16984   |           |           |          |              |
|               | 112 ->117 | 0.63158   |           |           |          |              |
| Excited State | 7:        | Singlet-A | 4.4752 eV | 277.05 nm | f=0.0878 | <S**2>=0.000 |
|               | 114 ->117 | 0.65591   |           |           |          |              |
|               | 115 ->118 | 0.20420   |           |           |          |              |
| Excited State | 8:        | Singlet-A | 4.5742 eV | 271.05 nm | f=0.0003 | <S**2>=0.000 |
|               | 108 ->116 | 0.41146   |           |           |          |              |
|               | 110 ->117 | -0.13730  |           |           |          |              |
|               | 113 ->121 | 0.11052   |           |           |          |              |
|               | 115 ->121 | 0.48783   |           |           |          |              |
| Excited State | 9:        | Singlet-A | 4.6414 eV | 267.13 nm | f=0.0101 | <S**2>=0.000 |
|               | 106 ->116 | 0.12815   |           |           |          |              |
|               | 109 ->116 | -0.18550  |           |           |          |              |
|               | 109 ->118 | 0.13277   |           |           |          |              |
|               | 110 ->117 | -0.29868  |           |           |          |              |
|               | 115 ->121 | -0.19295  |           |           |          |              |
|               | 115 ->122 | 0.47064   |           |           |          |              |

Excited State 10: Singlet-A 4.6461 eV 266.86 nm f=0.0082 <S\*\*2>=0.000

|           |          |
|-----------|----------|
| 106 ->116 | -0.20012 |
| 106 ->118 | -0.12800 |
| 108 ->116 | 0.11622  |
| 109 ->116 | -0.10730 |
| 109 ->117 | -0.13027 |
| 110 ->117 | 0.44322  |
| 112 ->116 | -0.10428 |
| 112 ->119 | -0.14130 |
| 115 ->122 | 0.34795  |

## Excitation energies and oscillator strengths for L (CH<sub>2</sub>Cl<sub>2</sub>)

Excited State 1: Singlet-A 3.4798 eV 356.30 nm f=1.5191 <S\*\*2>=0.000  
115 ->116 0.69292

Excited State 2: Singlet-A 3.8065 eV 325.72 nm f=0.0048 <S\*\*2>=0.000  
113 ->117 0.12093  
114 ->116 0.20966  
115 ->117 0.65955

Excited State 3: Singlet-A 4.0857 eV 303.46 nm f=0.2309 <S\*\*2>=0.000  
114 ->116 0.64492  
114 ->118 0.11557  
115 ->117 -0.23180

Excited State 4: Singlet-A 4.2688 eV 290.44 nm f=0.5146 <S\*\*2>=0.000  
114 ->117 -0.19146  
115 ->116 0.10590  
115 ->118 0.65960

Excited State 5: Singlet-A 4.2820 eV 289.54 nm f=0.0030 <S\*\*2>=0.000  
106 ->116 0.15256  
110 ->117 0.16750  
112 ->116 0.61118  
112 ->118 0.24021

Excited State 6: Singlet-A 4.3863 eV 282.66 nm f=0.0005 <S\*\*2>=0.000  
110 ->116 0.19519  
110 ->118 0.17621  
112 ->117 0.63104

Excited State 7: Singlet-A 4.4650 eV 277.68 nm f=0.0973 <S\*\*2>=0.000  
114 ->117 0.65808  
115 ->118 0.19715

Excited State 8: Singlet-A 4.5742 eV 271.05 nm f=0.0005 <S\*\*2>=0.000  
108 ->116 0.33799  
109 ->116 0.23815  
110 ->117 -0.15024  
113 ->121 0.10061  
115 ->121 0.47094  
115 ->122 0.15918

Excited State 9: Singlet-A 4.6354 eV 267.47 nm f=0.0143 <S\*\*2>=0.000  
108 ->116 0.12145  
109 ->116 -0.16270  
109 ->118 0.13166  
110 ->117 -0.22995

|           |          |
|-----------|----------|
| 115 ->121 | -0.26228 |
| 115 ->122 | 0.49269  |

Excited State 10: Singlet-A 4.6418 eV 267.10 nm f=0.0058 <S\*\*2>=0.000

|           |          |
|-----------|----------|
| 106 ->116 | -0.21769 |
| 106 ->118 | -0.14014 |
| 108 ->116 | 0.14004  |
| 110 ->117 | 0.49704  |
| 112 ->116 | -0.11709 |
| 112 ->119 | -0.15543 |
| 115 ->122 | 0.27763  |

## Excitation energies and oscillator strengths for **2** (CH<sub>2</sub>Cl<sub>2</sub>)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.1036 eV 399.49 nm f=0.6478 <S\*\*2>=0.000  
294 -> 295 -0.23695  
294 -> 296 0.65252

Excited State 2: Singlet-A 3.2633 eV 379.94 nm f=0.0100 <S\*\*2>=0.000  
294 -> 295 0.66372  
294 -> 296 0.23675

Excited State 3: Singlet-A 3.2841 eV 377.52 nm f=0.0800 <S\*\*2>=0.000  
293 -> 295 -0.67189  
293 -> 296 -0.15126

Excited State 4: Singlet-A 3.5382 eV 350.42 nm f=0.0463 <S\*\*2>=0.000  
291 -> 298 0.10382  
294 -> 297 -0.39183  
294 -> 298 0.56331

Excited State 5: Singlet-A 3.5853 eV 345.81 nm f=0.0000 <S\*\*2>=0.000  
293 -> 295 0.15756  
293 -> 296 -0.68721

Excited State 6: Singlet-A 3.6425 eV 340.38 nm f=1.0065 <S\*\*2>=0.000  
292 -> 295 0.68022  
292 -> 296 0.14806

Excited State 7: Singlet-A 3.6974 eV 335.33 nm f=0.0009 <S\*\*2>=0.000  
294 -> 297 0.58223  
294 -> 298 0.39731

Excited State 8: Singlet-A 3.7875 eV 327.35 nm f=0.0887 <S\*\*2>=0.000  
289 -> 295 -0.42420  
292 -> 297 0.27545  
292 -> 298 0.13889  
293 -> 297 -0.38968  
293 -> 298 -0.16685

Excited State 9: Singlet-A 3.8668 eV 320.64 nm f=0.0865 <S\*\*2>=0.000  
289 -> 295 -0.38685  
292 -> 297 0.10164  
293 -> 297 0.51649  
293 -> 298 0.18485

Excited State 10: Singlet-A 3.9071 eV 317.33 nm f=0.2500 <S\*\*2>=0.000  
288 -> 295 0.14041

|                   |           |                                           |
|-------------------|-----------|-------------------------------------------|
| 288 -> 296        | -0.38524  |                                           |
| 290 -> 295        | -0.11470  |                                           |
| 290 -> 296        | 0.32876   |                                           |
| 291 -> 295        | 0.11785   |                                           |
| 291 -> 296        | -0.36084  |                                           |
|                   |           |                                           |
| Excited State 11: | Singlet-A | 3.9275 eV 315.68 nm f=0.0165 <S**2>=0.000 |
| 292 -> 295        | -0.15316  |                                           |
| 292 -> 296        | 0.67940   |                                           |
|                   |           |                                           |
| Excited State 12: | Singlet-A | 3.9470 eV 314.12 nm f=0.3253 <S**2>=0.000 |
| 288 -> 296        | -0.25267  |                                           |
| 290 -> 296        | 0.22299   |                                           |
| 291 -> 295        | -0.18919  |                                           |
| 291 -> 296        | 0.53646   |                                           |
|                   |           |                                           |
| Excited State 13: | Singlet-A | 3.9954 eV 310.31 nm f=0.0007 <S**2>=0.000 |
| 293 -> 297        | 0.25664   |                                           |
| 293 -> 298        | -0.65535  |                                           |
|                   |           |                                           |
| Excited State 14: | Singlet-A | 4.0684 eV 304.75 nm f=0.0876 <S**2>=0.000 |
| 286 -> 295        | 0.27087   |                                           |
| 288 -> 295        | 0.16346   |                                           |
| 289 -> 295        | 0.28063   |                                           |
| 290 -> 295        | -0.12461  |                                           |
| 290 -> 296        | -0.15328  |                                           |
| 292 -> 297        | 0.43875   |                                           |
| 292 -> 298        | 0.20008   |                                           |
|                   |           |                                           |
| Excited State 15: | Singlet-A | 4.0712 eV 304.54 nm f=0.0121 <S**2>=0.000 |
| 285 -> 296        | 0.11175   |                                           |
| 288 -> 295        | -0.10100  |                                           |
| 288 -> 296        | 0.40836   |                                           |
| 290 -> 295        | -0.22330  |                                           |
| 290 -> 296        | 0.47780   |                                           |
|                   |           |                                           |
| Excited State 16: | Singlet-A | 4.0856 eV 303.47 nm f=0.0080 <S**2>=0.000 |
| 288 -> 295        | -0.39268  |                                           |
| 288 -> 296        | -0.12008  |                                           |
| 289 -> 295        | 0.21026   |                                           |
| 290 -> 295        | 0.33099   |                                           |
| 290 -> 296        | 0.14669   |                                           |
| 291 -> 295        | -0.30488  |                                           |
| 291 -> 296        | -0.10431  |                                           |
| 292 -> 297        | 0.16420   |                                           |
|                   |           |                                           |
| Excited State 17: | Singlet-A | 4.1254 eV 300.54 nm f=0.0651 <S**2>=0.000 |
| 285 -> 295        | 0.16189   |                                           |

|            |          |
|------------|----------|
| 286 -> 295 | -0.49717 |
| 287 -> 295 | 0.27962  |
| 291 -> 295 | 0.15458  |
| 292 -> 297 | 0.25554  |
| 292 -> 298 | 0.11041  |

Excited State 18: Singlet-A 4.1312 eV 300.12 nm f=0.6567 <S\*\*2>=0.000

|            |          |
|------------|----------|
| 294 -> 299 | 0.38304  |
| 294 -> 300 | 0.39003  |
| 294 -> 301 | -0.26953 |
| 294 -> 302 | -0.26405 |

Excited State 19: Singlet-A 4.1480 eV 298.90 nm f=0.0106 <S\*\*2>=0.000

|            |          |
|------------|----------|
| 288 -> 295 | 0.20298  |
| 290 -> 295 | -0.23939 |
| 291 -> 295 | -0.55842 |
| 291 -> 296 | -0.19291 |

Excited State 20: Singlet-A 4.1542 eV 298.46 nm f=0.0035 <S\*\*2>=0.000

|            |          |
|------------|----------|
| 286 -> 296 | -0.11277 |
| 287 -> 295 | 0.10280  |
| 289 -> 295 | -0.11964 |
| 289 -> 296 | 0.64132  |
| 290 -> 296 | -0.12095 |