# Supporting Information (SI)

## High contrast off-on fluorescence photo-switching *via* copper ion recognition, *trans-cis* isomerization and ring closure of a thiosemicarbazide Schiff base

Wei Li[a], Xiaoping Gan[a, b], Dan Liu[a], Xiaohe Tian[c], Jianhua Yu[a], Jieying Wu[a], Yupeng Tian[a], Hongping Zhou[a,*]

[a]*College of Chemistry and Chemical Engineering, Anhui University and Key Labotatory of Functional Inorganic Materials Chemistry of Anhui Province, 230601, Hefei, P.R. China*

[b]*Department of Applied Chemistry, School of Science, Anhui Agricultural University, Hefei, 230036, P. R. China.*

[c]*School of Life Sciences, Anhui University, Hefei 230601, P. R. China.*

Corresponding author. Fax: +86-551-63861279; Tel: +86-551--63861279

E-mail: zhpzhp@263.net

**Figure S1** (a) The UV-visible spectrum of photo stability for compound Lo in acetonitrile (under visible light); (b) The UV-visible spectroscopy of photo stability for compound Lo in tetrahydrofuran (under dark light).

**Figure S2** (a) Fluorescence response of **Lo** (10 μM) to 10 μM of other metal ions (the blue bar portion) and to the mixture of other metal ions with 10 μM of $Cu^{2+}$ (the red bar portion) in $CH_3CN$ at $\lambda_{ex}$ = 475 nm.

**Figure S3** Job plot of **Lo** and $Cu^{2+}$ in $CH_3CN$ at $\lambda_{ex}$ = 475 nm. The total concentration of **Lo** and $Cu^{2+}$ was 10 μM.

**Figure S4** The linear plot between amounts of $Cu^{2+}$ ion and fluorescent intensity. $F_0$ and F are the emission intensities of Lo in the absence and presence of $Cu^{2+}$, respectively. (a) Benesi-

Hildebrand plot for the determination of stability constant of **Lo**-$Cu^{2+}$ in $CH_3CN$ solution at $\lambda_{ex}$ = 475 nm; (b) calibration curve for the detection limit of **Lo**-$Cu^{2+}$ in $CH_3CN$ solution at $\lambda_{ex}$ = 475 nm.

**Figure S5** Fluorescence intensity of free **Lo** (10 μM) at various different pH in the absence and presence of $Cu^{2+}$ in $CH_3CN$ at $\lambda_{ex}$ = 475 nm.

**Figure S6** Reversibility experiment from fluorescence spectra of **Lo** in the presence of $Cu^{2+}$ (1.0 equiv.) or $Na_2S$ (1.0 equiv.) in $CH_3CN$ at $\lambda_{ex}$ = 475 nm.

**Figure S7** The changes in fluorescent spectrum of **Lo** (10 μM) with the increasing time after the addition of $Cu^{2+}$ (10 μM) in $CH_3CN$ at $\lambda_{ex}$ = 475 nm.

**Figure S8** MTT assay of **Lo** on HepG2 cell over 48 hours.

**Figure S9** Photon-bleach experiment showed **Lo (**100 μM) photostability over continued laser scanning.

**Figure S10** Absorption (a) and Fluorescent (c) spectra of **Lo** in different solution before visible light irradiation for ten minutes; Absorption (b) and Fluorescent (d) spectra of **Lo** in different solution after visible light irradiation for ten minutes.

**Figure S11** Mass spectrum of (a) **Lo** in THF solution (10 μM) and (b) **Lo** under the visible light irradiation in THF solution (10 μM)

**Figure S12** Development of photoluminescence spectra of **Lo** in THF (10 μM) with the increasing illumination time (0-10 minutes) by visible light irradiation.

**Figure S13** The normalized fluorescence lifetime for **Lo** before (red) and after (blue) irradiation by visible light in THF solution.

**Figure S14** Bar diagrams showing the cytotoxicity of the compound **Lo** in HeLa cells upon photo-irradiation with visible light (400–700 nm,10 J $cm^{-2}$, red bars) and in dark (black bars) as determined from MTT assay.

**Figure S15** The normalized fluorescence lifetime for **Lo-*trans*** and **Lo-*cis*** in solid state.

**Figure S16** Changes in $^{13}C$ NMR spectrum of **Lo** before and after the visible light irradiation in solid state

**Figure S17** $^{1}H$ NMR spectrum of **2** (in DMSO-$d_6$)

**Figure S18** $^{13}C$ NMR spectrum of **2** (in DMSO-$d_6$)

**Figure S19** Mass spectrum of **2**

**Figure S20** $^{1}$H NMR spectrum of **Lo** (in DMSO-$d_6$)

**Figure S21** $^{13}$C NMR spectrum of **Lo** (in $CDCl_3$-$d_1$)

**Figure S22** Mass spectrum of **Lo**

**Figure S23** FT-IR of **Lo** in KBr

**Table S1** Photophysical data of **Lo** in nine different solvents.

**Table S2** Quantum yields and fluorescence lifetimes of **Lo** in THF solvent.

**Table S3** Quantum yields and fluorescence lifetimes of **Lo-*trans* and Lo-*cis*.**

**Table S4** The corresponding DFT coordinates for the optimized structures of Lo-***trans***

**Table S5** The corresponding DFT coordinates for the optimized structures of **Lo-*cis***

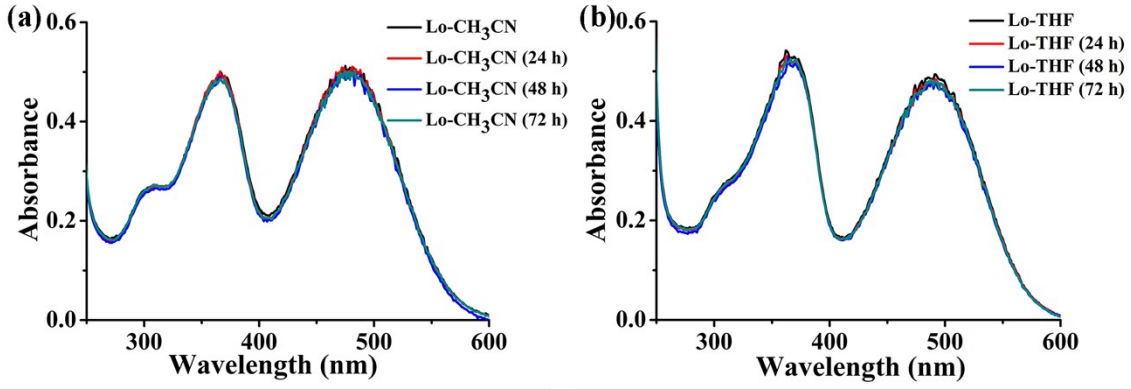


**Figure S1** (a) The UV-visible spectrum of photo stability for compound Lo in acetonitrile (under visible light); (b) The UV-visible spectroscopy of photo stability for compound Lo in tetrahydrofuran (under dark light).

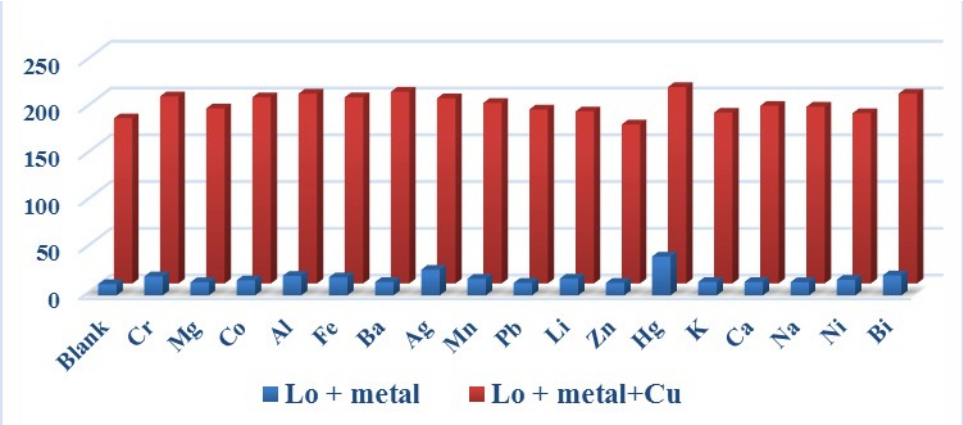


**Figure S2** (a) Fluorescence response of **Lo** (10 μM) to 10 μM of other metal ions (the blue bar portion) and to the mixture of other metal ions with 10 μM of $Cu^{2+}$ (the red bar portion) in $CH_3CN$ at $\lambda_{ex}$ = 475 nm.

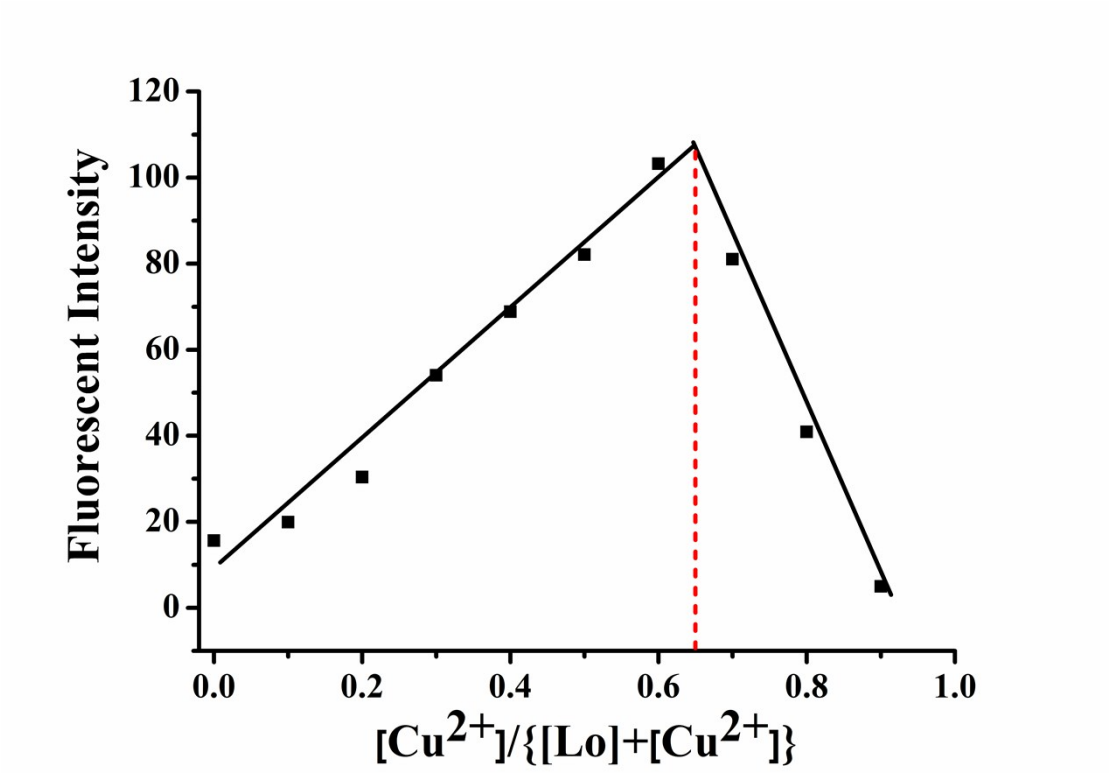


**Figure S3** Job plot of **Lo** and $Cu^{2+}$ in $CH_3CN$ at $\lambda_{ex}$ = 475 nm. The total concentration of **Lo** and $Cu^{2+}$ was 10 μM.

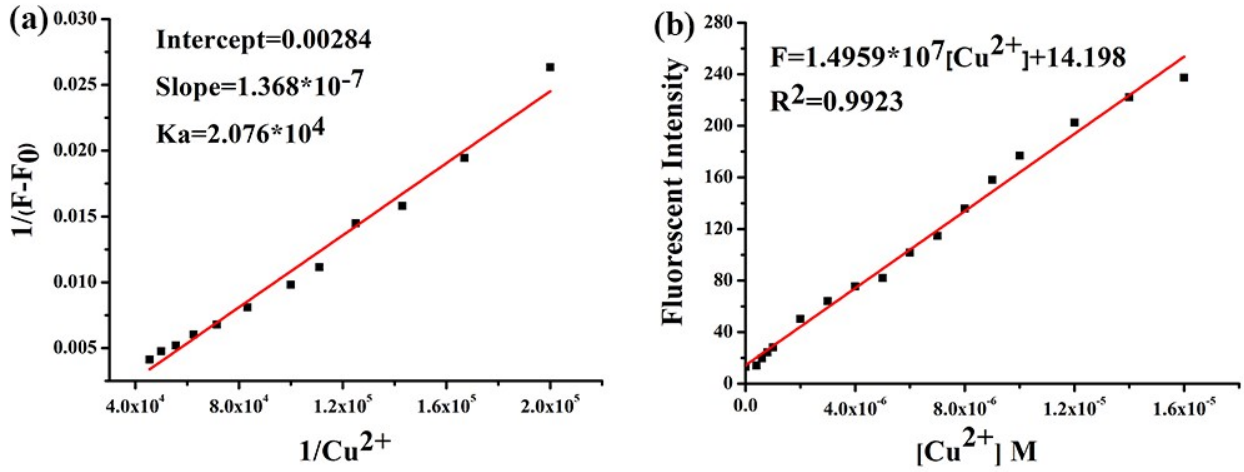


**Figure S4** The linear plot between amounts of $Cu^{2+}$ ion and fluorescent intensity. $F_0$ and F are the emission intensities of **Lo** in the absence and presence of $Cu^{2+}$, respectively. (a) Benesi-Hildebrand plot for the determination of stability constant of **Lo**-$Cu^{2+}$ in $CH_3CN$ solution at $\lambda_{ex}$ = 475 nm; (b) calibration curve for the detection limit of **Lo**-$Cu^{2+}$ in $CH_3CN$ solution at $\lambda_{ex}$ = 475 nm.

The detection limit (DL) of $Cu^{2+}$ ions using probe Lo was determined from the following equation: DL = K × SD/S, where K = 3; SD is the standard deviation of the blank solution; S is the slope of the calibration curve.

Probe **Lo** for $Cu^{2+}$: DL = K×SD/S = 3×2.132/1.4959×$10^7$ = 4.275×$10^{-7}$ M.

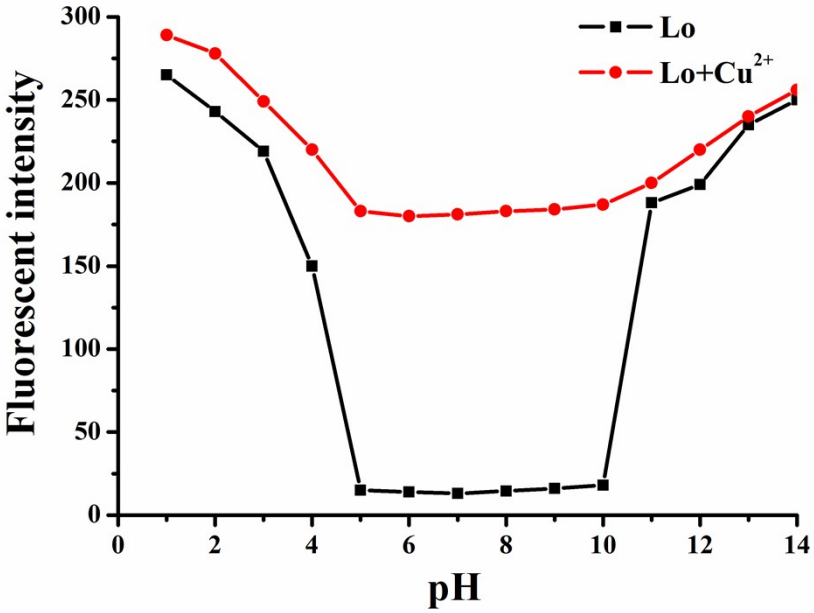


**Figure S5** Fluorescence intensity of free **Lo** (10 μM) at various different pH in the absence and presence of $Cu^{2+}$ in $CH_3CN$ at $\lambda_{ex}$ = 475 nm.

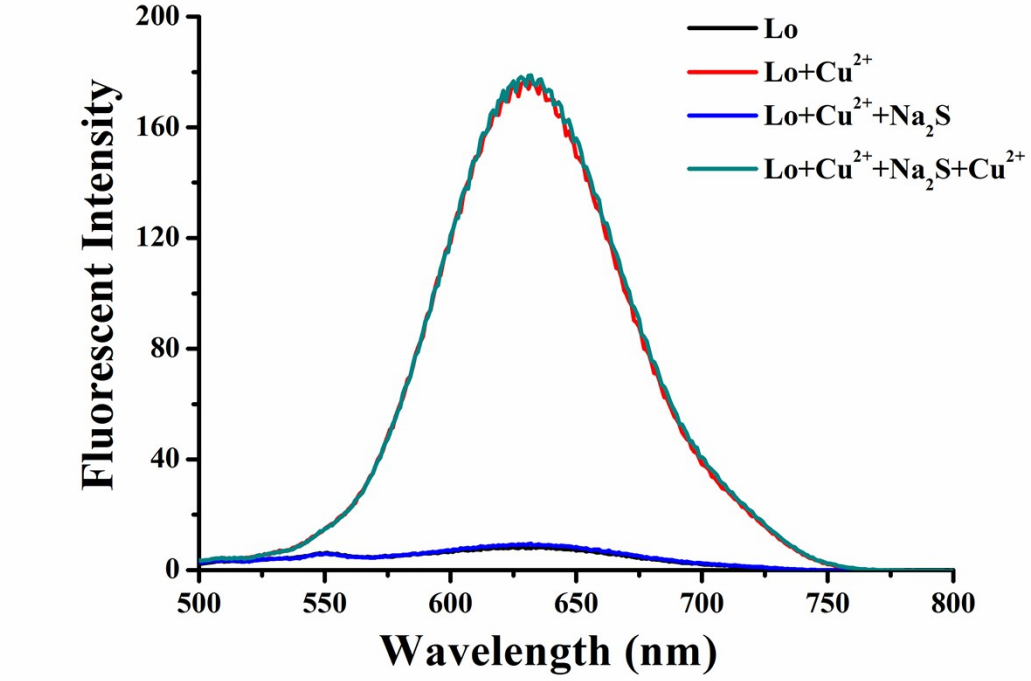


**Figure S6** Reversibility experiment from fluorescence spectra of **Lo** in the presence of $Cu^{2+}$ (1.0 equiv.) or $Na_2S$ (1.0 equiv.) in $CH_3CN$ at $\lambda_{ex}$ = 475 nm.

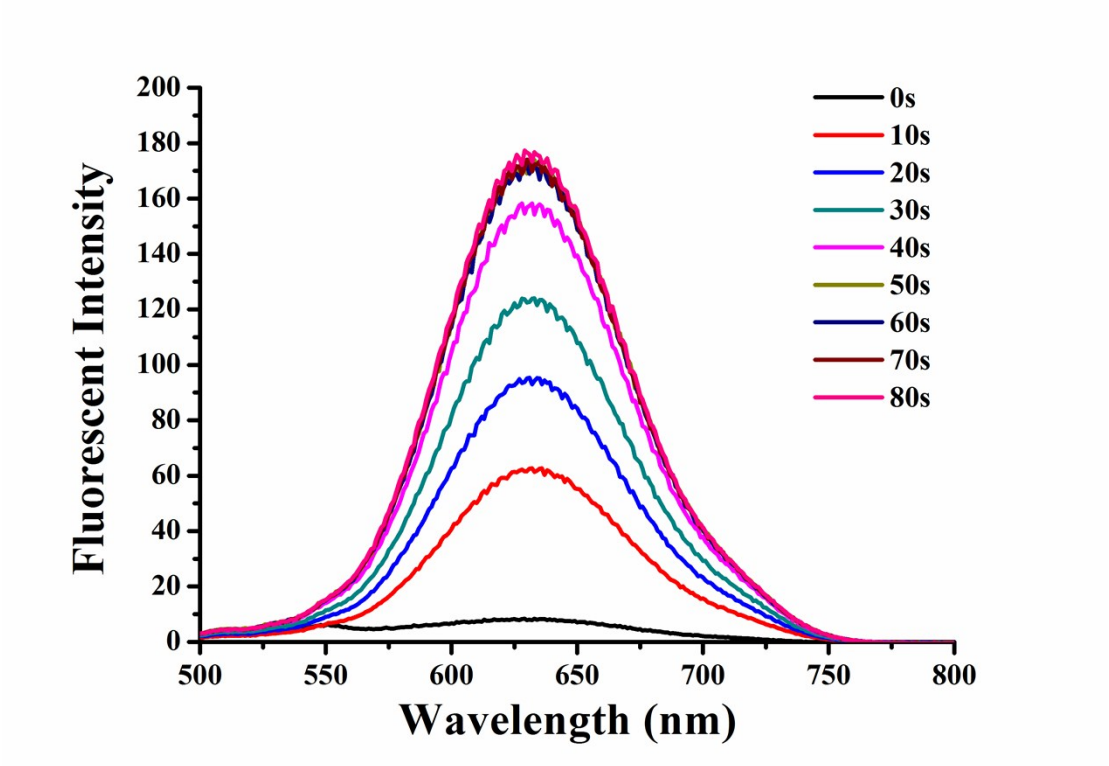


**Figure S7** The changes in fluorescent spectrum of **Lo** (10 μM) with the increasing time after the addition of $Cu^{2+}$ (10 μM) in $CH_3CN$ at $\lambda_{ex}$ = 475 nm.

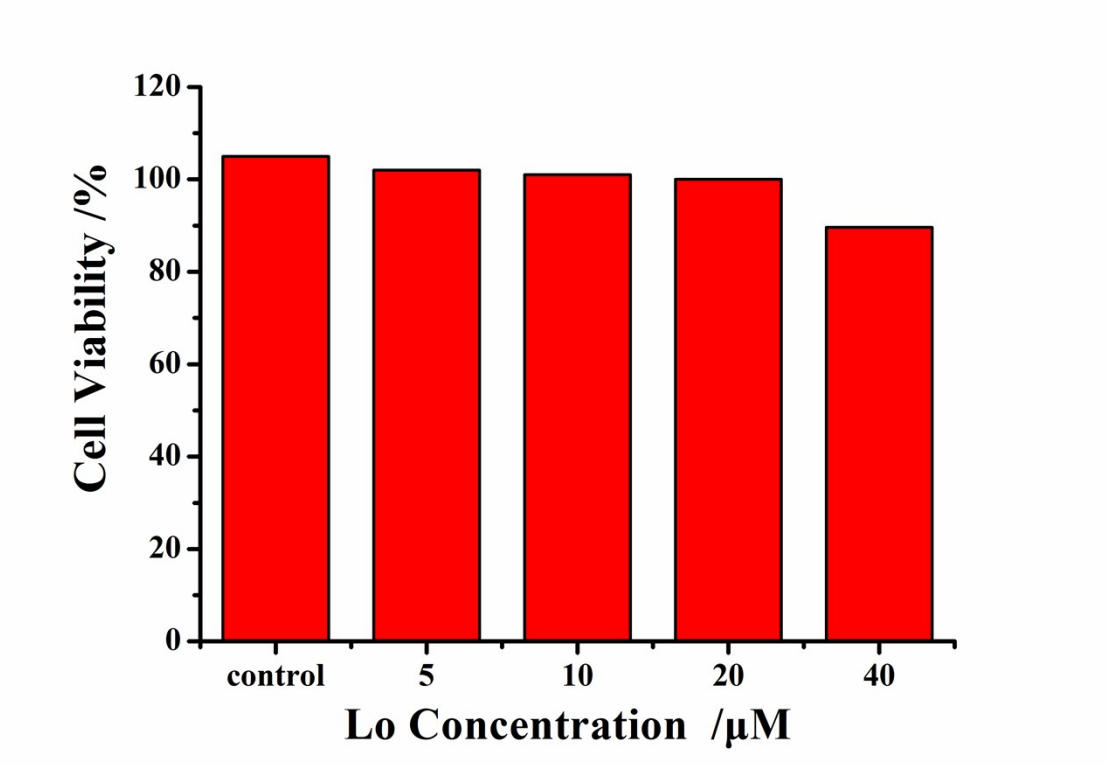


**Figure S8** MTT assay of **Lo** on HepG2 cell over 24 hours.

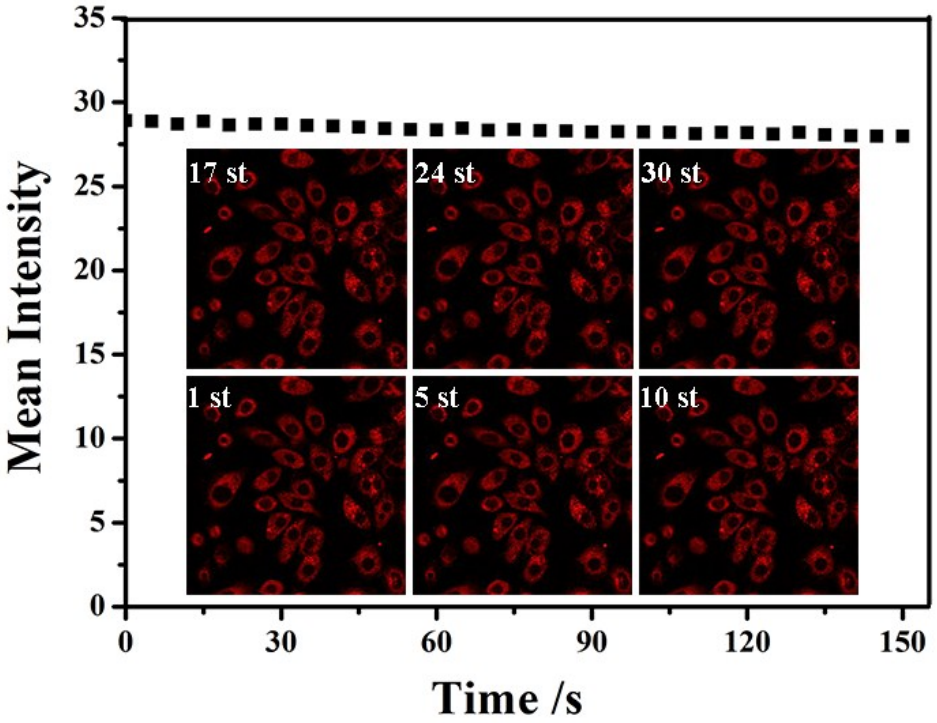


**Figure S9** Photon-bleach experiment showed **Lo (**100 μM) photostability over continued laser scanning.

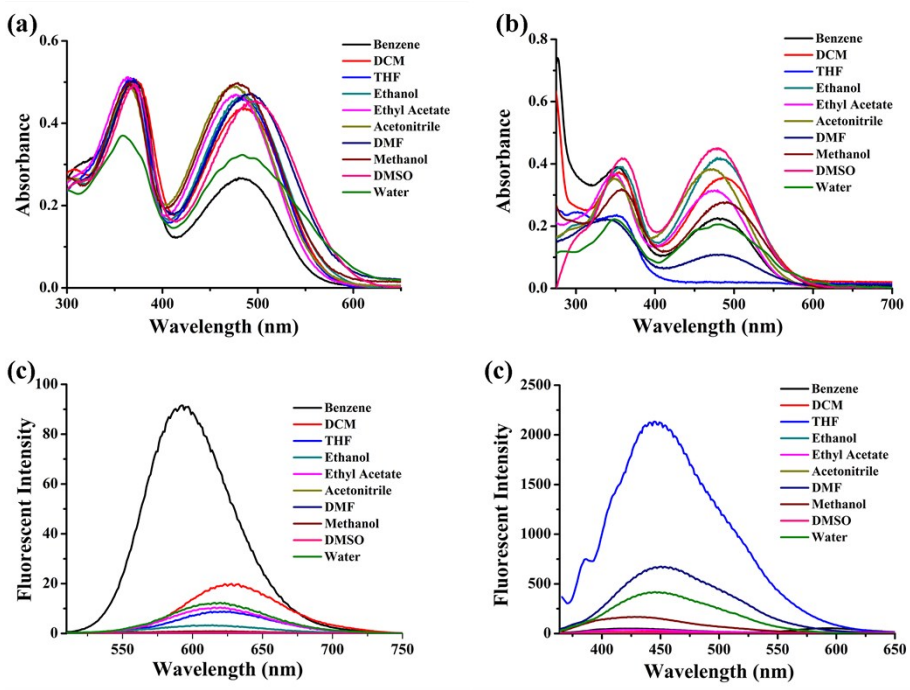


**Figure S10** Absorption (a) and Fluorescent (c) spectra of **Lo** in different solution before visible light irradiation for ten minutes; Absorption (b) and Fluorescent (d) spectra of **Lo** in different solution after visible light irradiation for ten minutes.

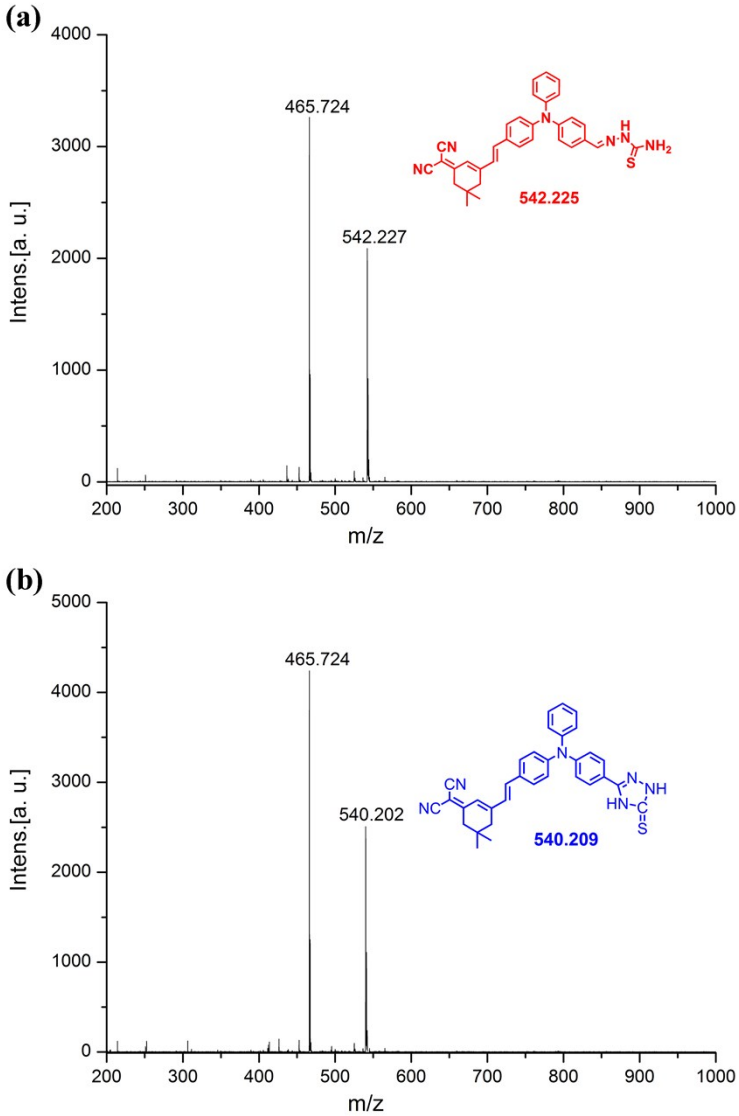


**Figure S11** Mass spectrum of (a) **Lo** in THF solution (10 μM) and (b) **Lo** under the visible light irradiation in THF solution (10 μM)

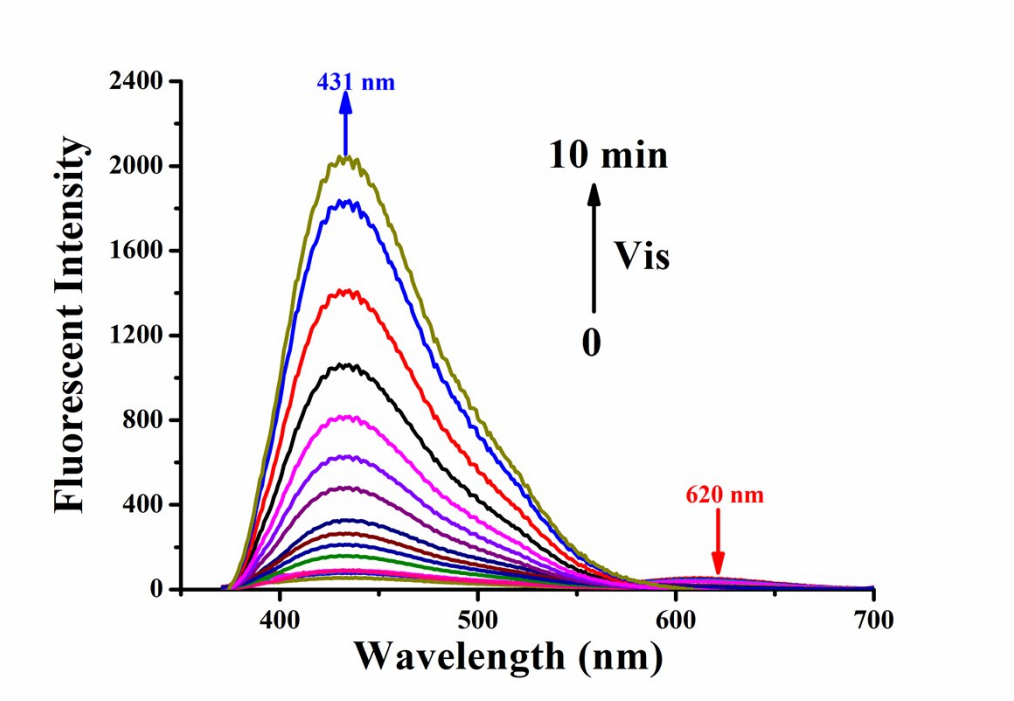


**Figure S12** Development of photoluminescence spectra of **Lo** in THF (10 μM) with the increasing illumination time (0-10 minutes) by visible light irradiation.

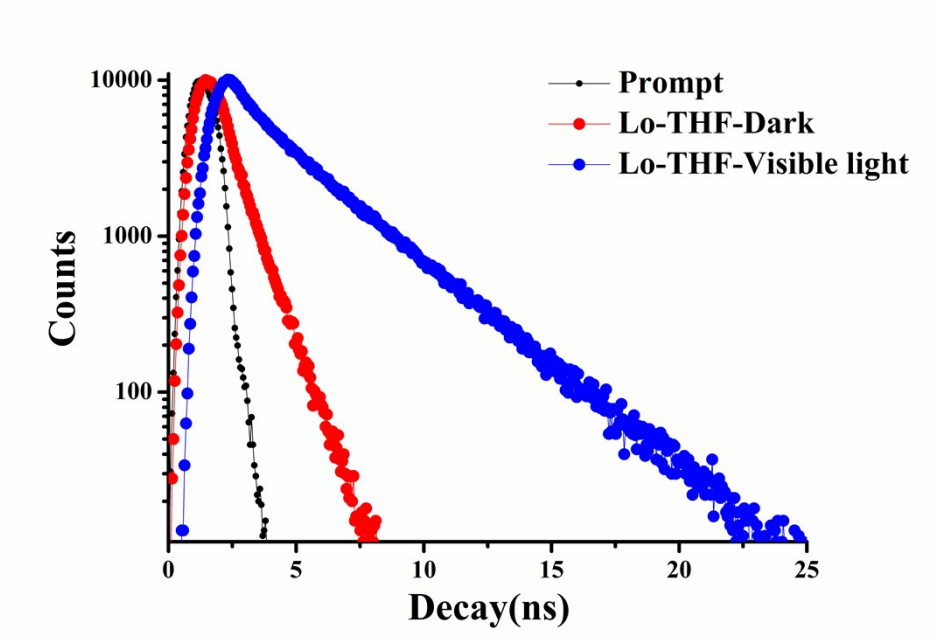


**Figure S13** The normalized fluorescence lifetime for **Lo** before (red) and after (blue) irradiation by visible light in THF solution.

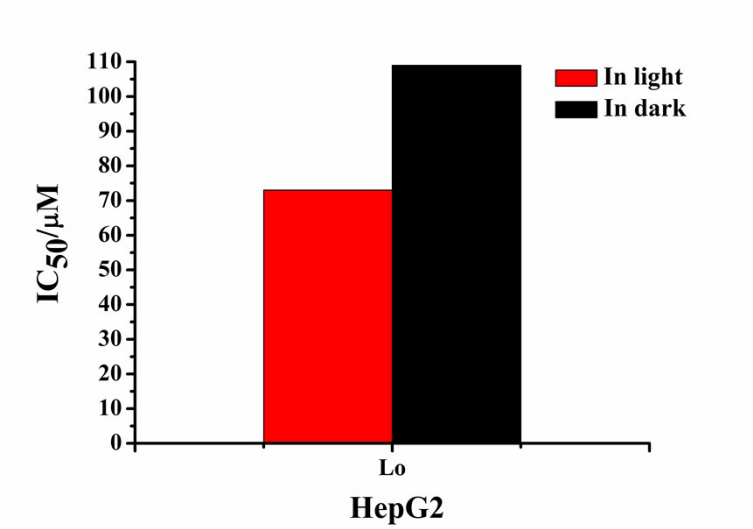


**Figure S14** Bar diagrams showing the cytotoxicity of the compound **Lo** in HepG2 cells upon photo-irradiation with visible light (400–700 nm,10 J $cm^{-2}$, red bars) and in dark (black bars) as determined from MTT assay.

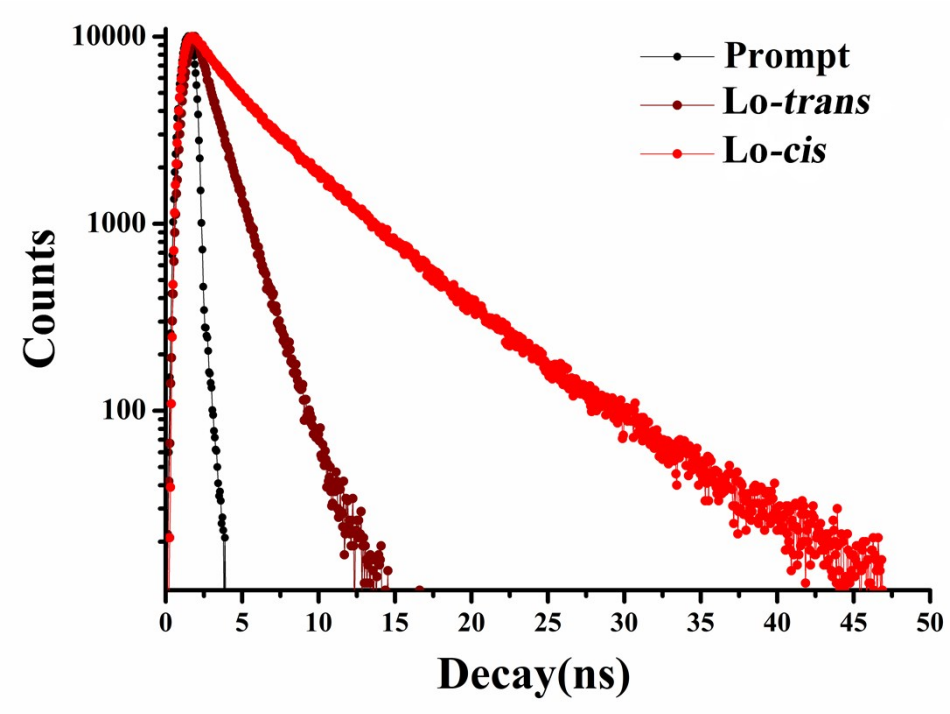


**Figure S15** The normalized fluorescence lifetime for **Lo-*trans*** and **Lo-*cis*** in solid state.

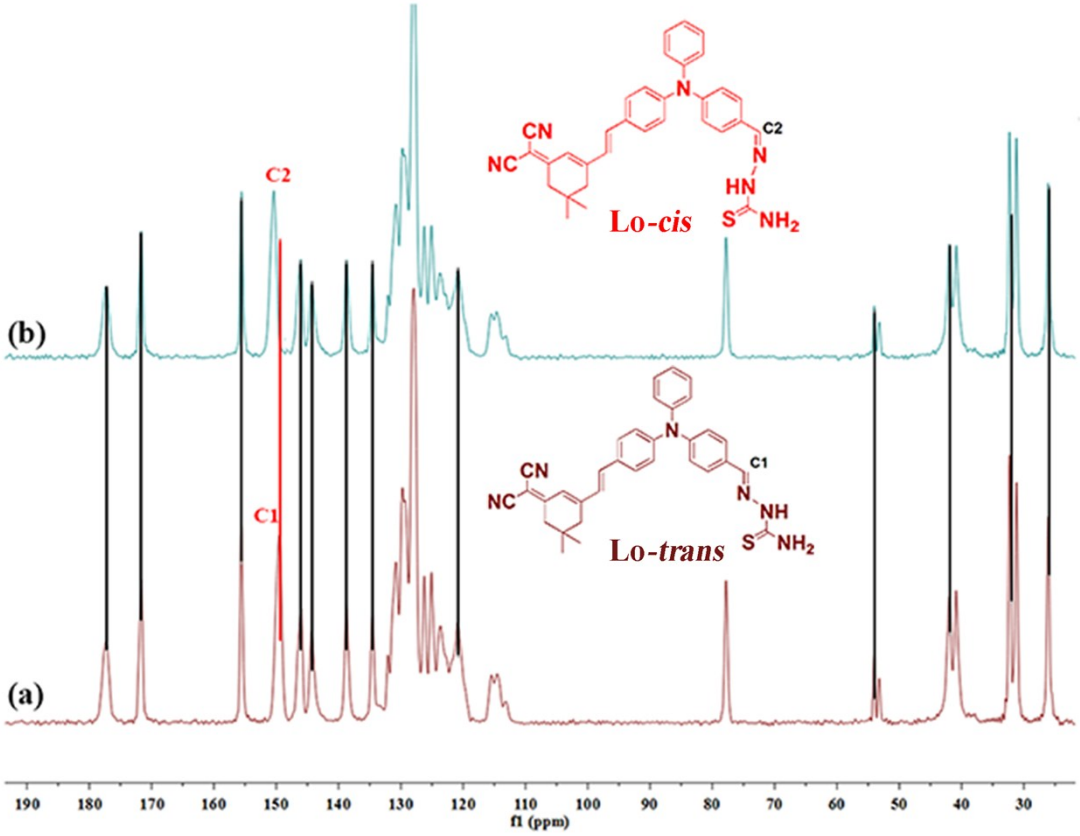


**Figure S16** Changes in $^{13}C$ NMR spectrum of **Lo** before and after the visible light irradiation in solid state

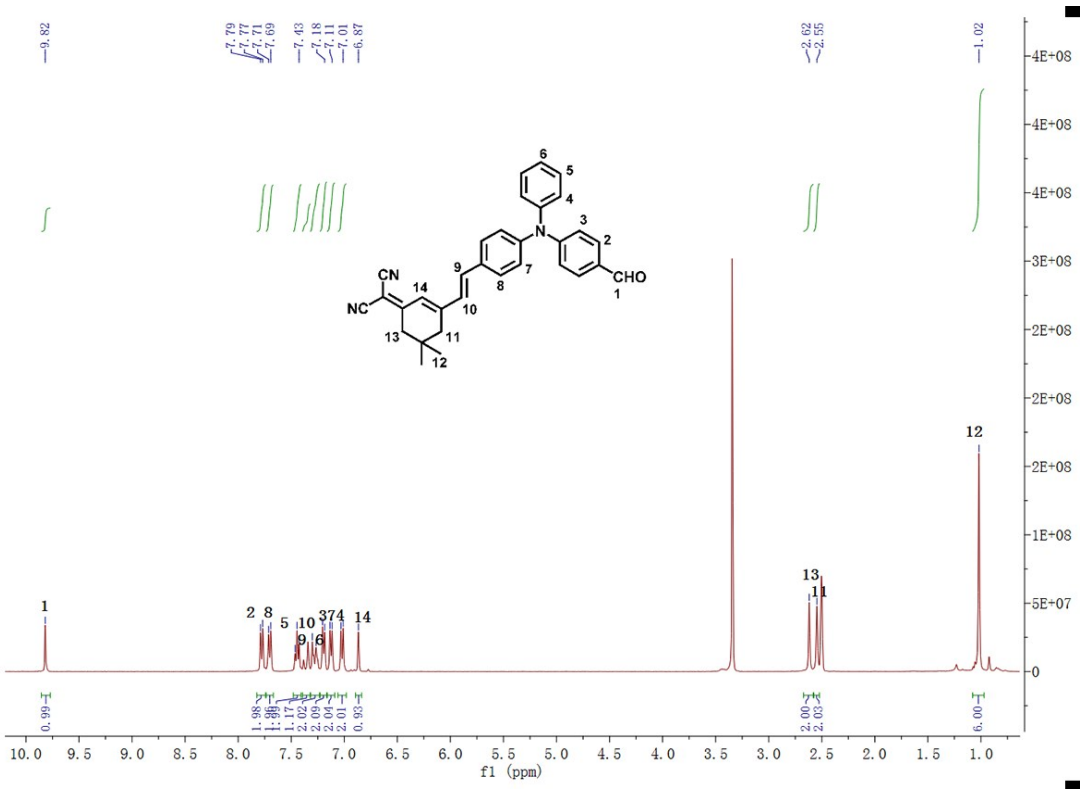


**Figure S17** $^{1}$H NMR spectrum of **2** (in DMSO-$d_6$)

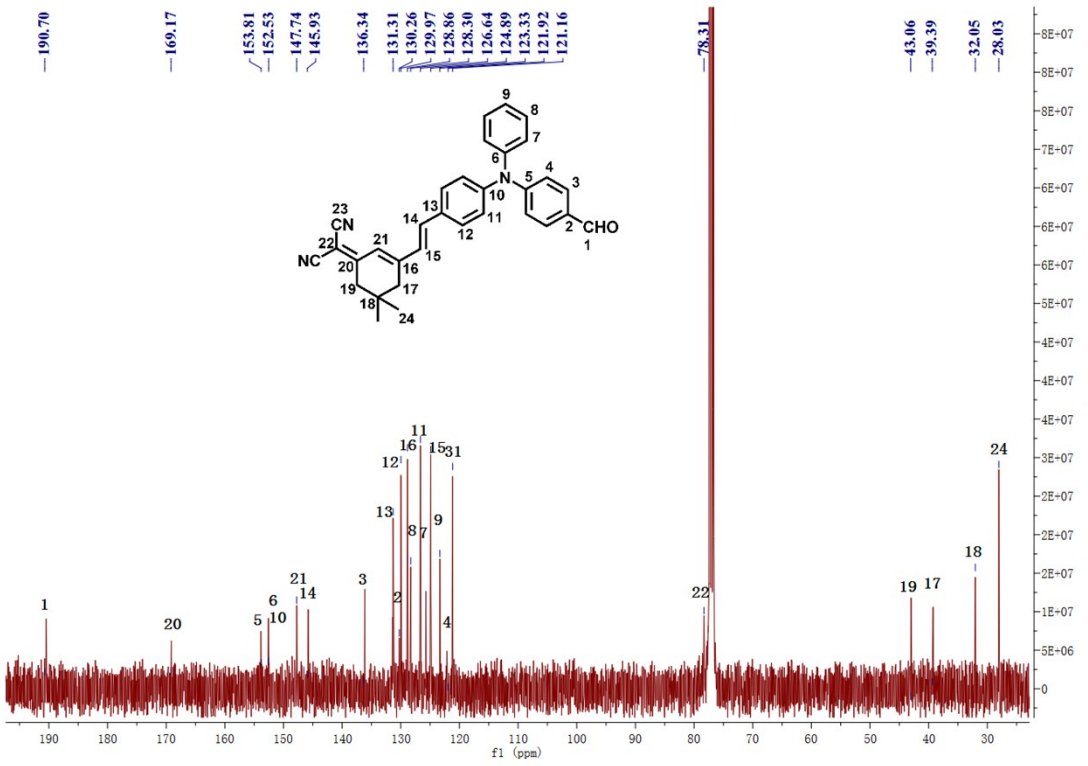


**Figure S18** $^{13}$C NMR spectrum of **2** (in DMSO-$d_6$)

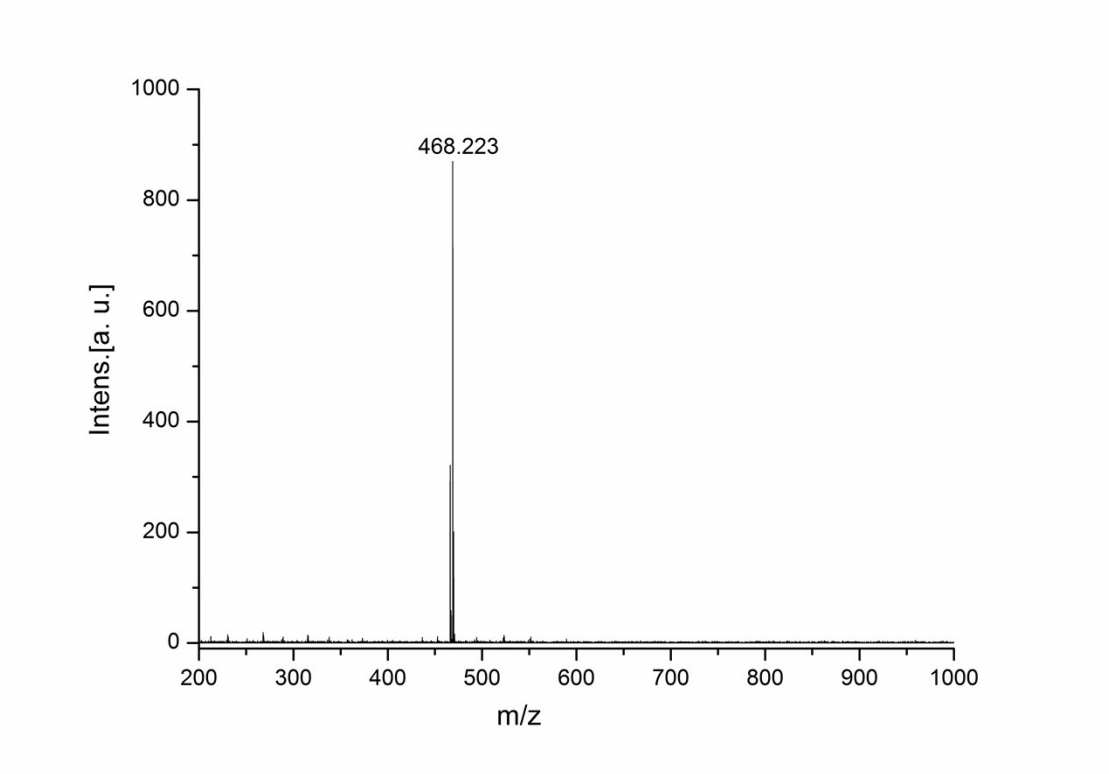


**Figure S19** Mass spectrum of **2**

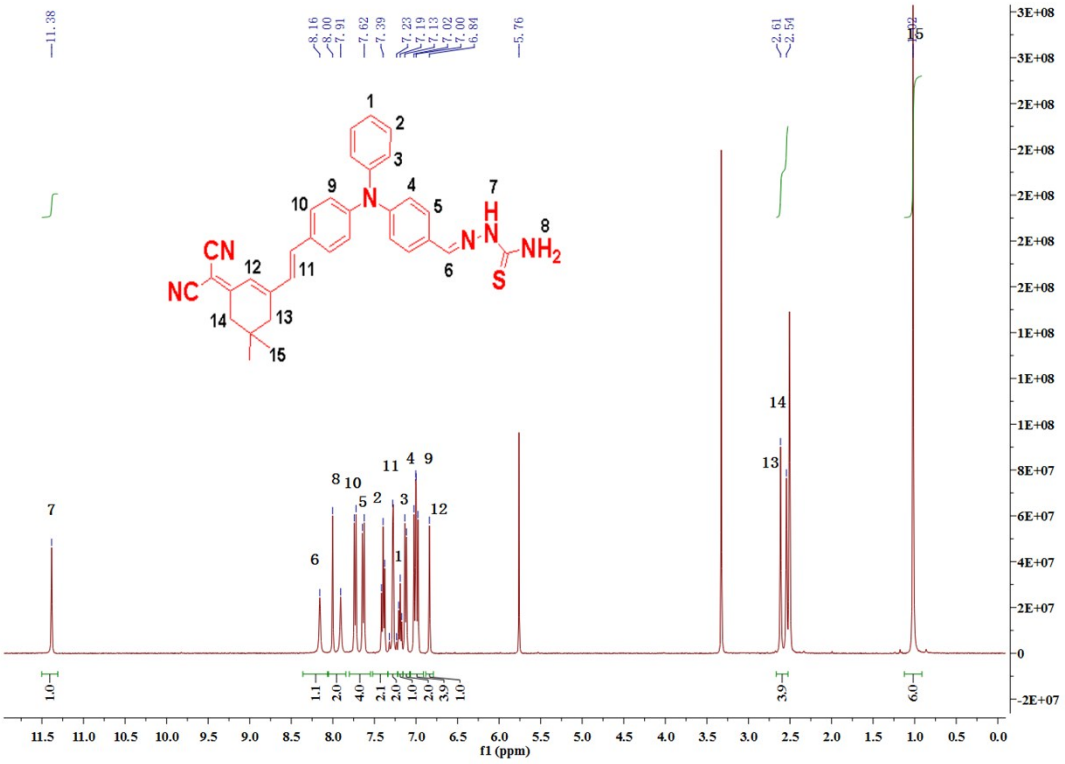


**Figure S20** $^{1}$H NMR spectrum of **Lo** (in DMSO-$d_6$)

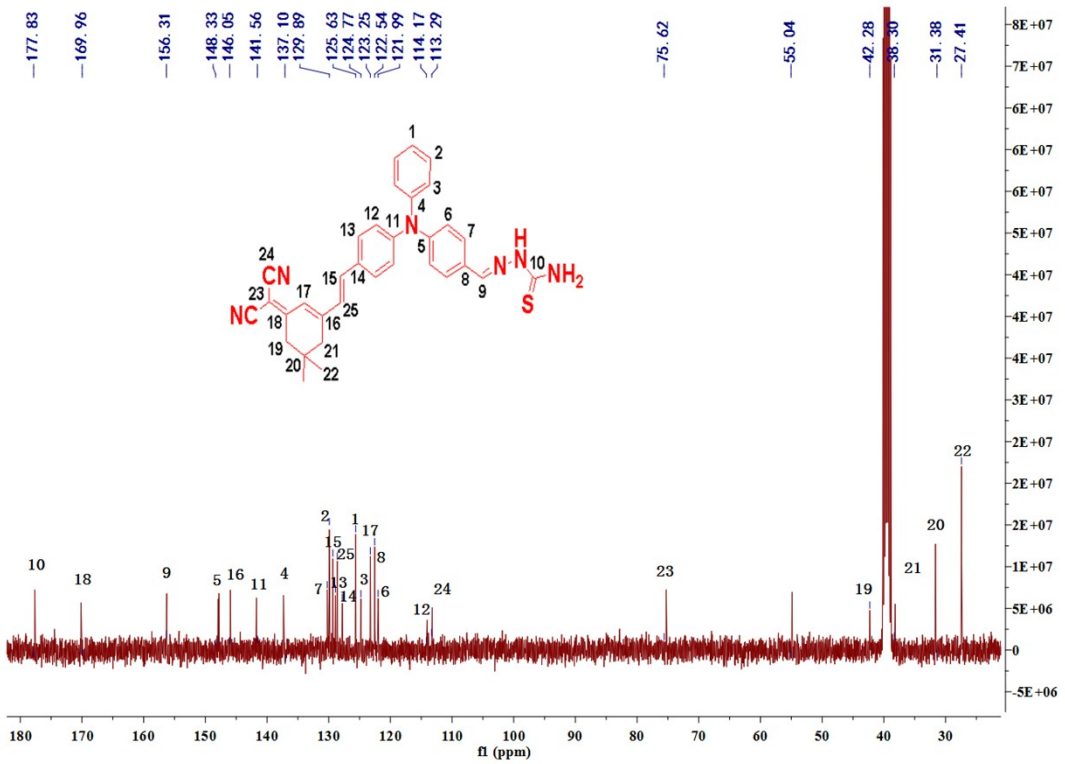


**Figure S21** $^{13}$C NMR spectrum of **Lo** (in $CDCl_3$-$d_1$)

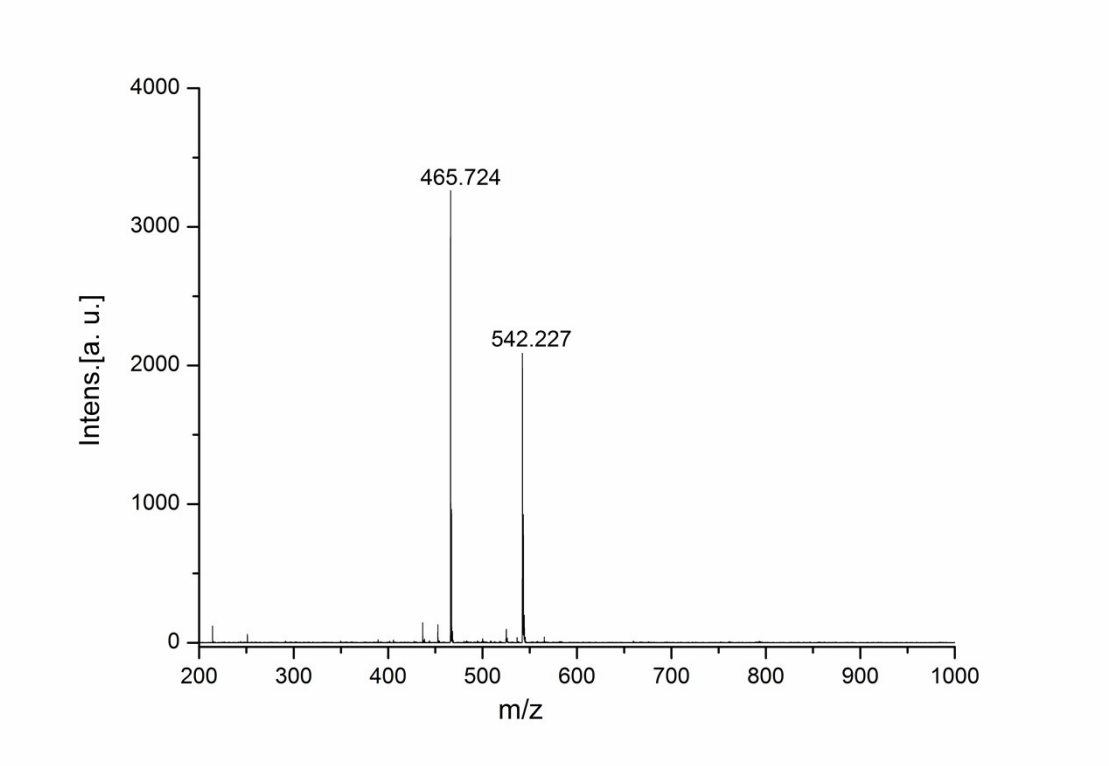


**Figure S22** Mass spectrum of **Lo**

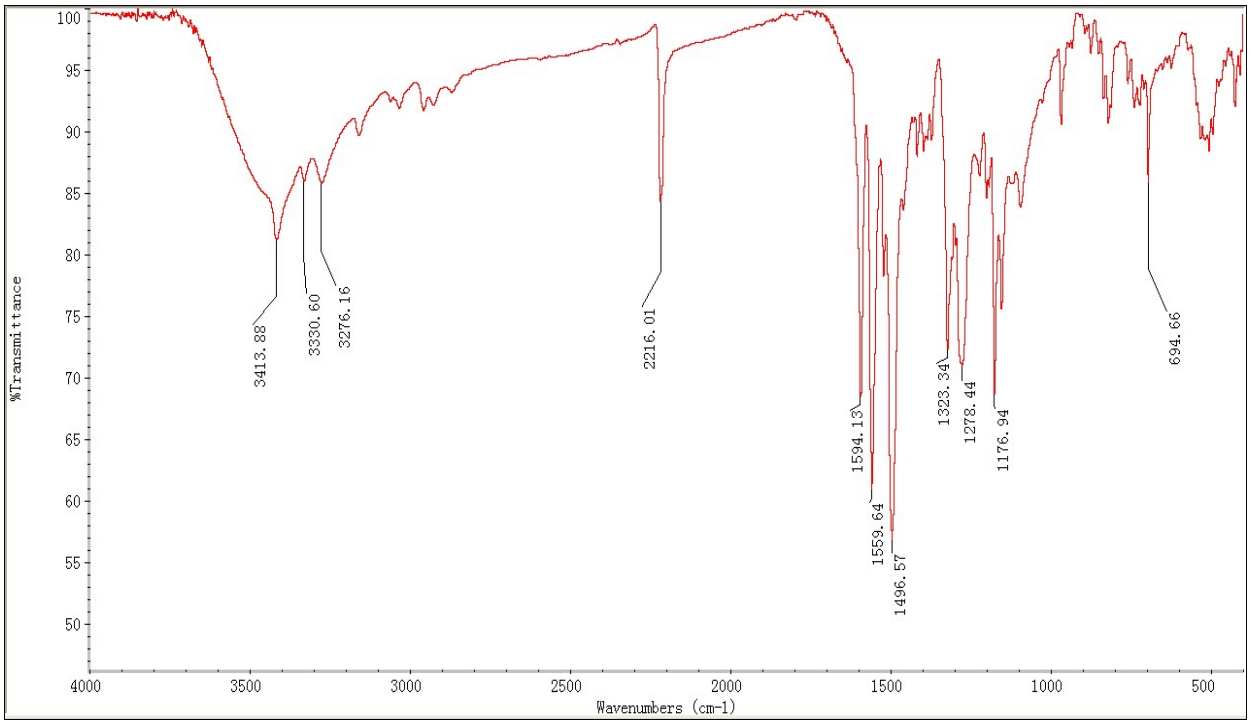


**Figure S23** FT-IR of **Lo** in KBr

**Table S1** Photophysical data of **Lo** in nine different solvents.

**Table 1.** Photophysical data of **Lo** in nine different solvents.

| Compound | Solvents | $\lambda_{max}$ [a] | $\lambda_{max}$ [b] | $\lambda_{max}$ [c] | $\lambda_{max}$ [d] |
|---|---|---|---|---|---|
| **Lo** | Benzene | 368, 483 | 593 | 352, 483 | 422, 594 |
| | DCM | 370, 485 | 623 | 352, 484 | 436, 619 |
| | THF | 368, 484 | 624 | 353 | 444 |
| | Ethanol | 365, 484 | 611 | 356, 481 | 430, 619 |
| | Ethyl acetate | 363, 477 | 620 | 349, 476 | 424, 608 |
| | Acetonitrile | 366, 476 | 616 | 346, 472 | 424, 620 |
| | DMF | 369, 493 | 616 | 345, 484 | 452 |
| | Methanol | 364, 478 | 614 | 357, 488 | 425 |
| | DMSO | 372, 498 | 621 | 360, 488 | 397 |
| | Water | 359, 485 | 618 | 349, 484 | 440 |

[a] Absorption peak position in nm ($c$ =1.0 ×$10^{-5}$ mol $L^{-1}$), [b] Peak position of SPEF in nm ($c$ =1.0 ×$10^{-5}$ mol $L^{-1}$), excited at the absorption maximum, [c] Absorption peak position in nm ($c$ =1.0 ×$10^{-5}$ mol $L^{-1}$) after vis irradiation, [d] Peak position of SPEF in nm ($c$ =1.0 ×$10^{-5}$ mol $L^{-1}$) after vis irradiation, excited at the absorption maximum,

**Table S2** Quantum yields and fluorescence lifetimes of **Lo** in THF solvent.

**Table S2.** Quantum yields and fluorescence lifetimes of **Lo** in THF solvent.

| Compound | Solvents | $\Phi$ [a] (%) | $\langle\tau\rangle$[b] (ns) | $\Phi$ [c] (%) | $\langle\tau\rangle$[d] (ns) |
|---|---|---|---|---|---|
| **Lo** | THF | -- | 0.21 | 13.9 | 7.7 |

[a] Quantum yields before vis irradiation, [b] Weighted mean lifetime before vis irradiation, [c] Quantum yields after vis irradiation, [d] Weighted mean lifetime after vis irradiation.

**Table S3** Quantum yields and fluorescence lifetimes of **Lo-*trans* and Lo-*cis*.**

**Table S3.** Quantum yields and fluorescence lifetimes of **Lo-*trans* and Lo-*cis***.

| Compound | $\Phi$ (%) | $<\tau>$ (ns) |
|---|---|---|
| Lo-trans | -- | 0.32 |
| Lo-cis | 15.2 | 9.1 |

**Table S4** The corresponding DFT coordinates for the optimized structures of **Lo-*trans***

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -2.367178 | -2.482343 | -0.100625 |
| 2 | 6 | 0 | -1.099187 | -2.691047 | -0.279890 |
| 3 | 6 | 0 | -3.194796 | -3.476945 | -0.011331 |
| 4 | 6 | 0 | -2.802434 | -1.263974 | 0.003255 |
| 5 | 6 | 0 | -4.057727 | -0.888185 | -0.336229 |
| 6 | 6 | 0 | -4.512637 | 0.372850 | -0.253599 |
| 7 | 6 | 0 | -3.731838 | 1.371320 | 0.190417 |
| 8 | 6 | 0 | -2.484947 | 1.033281 | 0.555327 |
| 9 | 6 | 0 | -2.051049 | -0.233724 | 0.459566 |
| 10 | 6 | 0 | -0.448396 | -3.825872 | 0.067591 |
| 11 | 6 | 0 | 0.871557 | -4.019131 | -0.094864 |
| 12 | 6 | 0 | 1.669824 | -3.050433 | -0.574550 |
| 13 | 6 | 0 | 1.038081 | -1.956598 | -1.025105 |
| 14 | 6 | 0 | -0.283688 | -1.789485 | -0.873830 |
| 15 | 6 | 0 | -4.354188 | -3.411371 | 0.687464 |
| 16 | 6 | 0 | -5.219194 | -4.431621 | 0.803374 |
| 17 | 6 | 0 | -4.966192 | -5.601249 | 0.204906 |
| 18 | 6 | 0 | -3.836584 | -5.716657 | -0.503001 |
| 19 | 6 | 0 | -2.987383 | -4.680660 | -0.596968 |
| 20 | 6 | 0 | -4.187464 | 2.636882 | 0.251917 |
| 21 | 7 | 0 | -3.527792 | 3.640350 | 0.647400 |
| 22 | 7 | 0 | -4.061665 | 4.883466 | 0.622307 |
| 23 | 6 | 0 | 3.000811 | -3.227240 | -0.680105 |
| 24 | 6 | 0 | 3.997788 | -2.326507 | -0.784254 |
| 25 | 6 | 0 | 4.071548 | -1.038456 | -0.371384 |
| 26 | 6 | 0 | 2.993502 | -0.370262 | 0.459471 |
| 27 | 6 | 0 | 5.213088 | -0.351301 | -0.596035 |

| | | | | | |
|---|---|---|---|---|---|
| 28 | 6 | 0 | 5.480525 | 0.885880 | -0.125549 |
| 29 | 6 | 0 | 4.471912 | 1.576400 | 0.774516 |
| 30 | 6 | 0 | 3.579327 | 0.572365 | 1.522240 |
| 31 | 6 | 0 | 6.638102 | 1.512068 | -0.429154 |
| 32 | 6 | 0 | 2.435012 | 1.315177 | 2.244522 |
| 33 | 6 | 0 | 4.388795 | -0.218745 | 2.570976 |
| 34 | 6 | 0 | -4.001427 | 5.675268 | -0.499062 |
| 35 | 16 | 0 | -4.579791 | 7.142210 | -0.498280 |
| 36 | 7 | 0 | -3.423546 | 5.138826 | -1.621982 |
| 37 | 6 | 0 | 7.570477 | 0.980170 | -1.195834 |
| 38 | 7 | 0 | 8.394108 | 0.518769 | -1.868330 |
| 39 | 6 | 0 | 6.893554 | 2.722725 | 0.028183 |
| 40 | 7 | 0 | 7.114026 | 3.786282 | 0.432565 |
| 41 | 1 | 0 | -4.770006 | -1.597644 | -0.792314 |
| 42 | 1 | 0 | -5.543011 | 0.581908 | -0.591456 |
| 43 | 1 | 0 | -1.789667 | 1.790558 | 0.957144 |
| 44 | 1 | 0 | -1.031600 | -0.389487 | 0.854988 |
| 45 | 1 | 0 | -0.956971 | -4.645271 | 0.603591 |
| 46 | 1 | 0 | 1.309769 | -4.967246 | 0.264463 |
| 47 | 1 | 0 | 1.593893 | -1.190756 | -1.589647 |
| 48 | 1 | 0 | -0.677989 | -0.871080 | -1.343228 |
| 49 | 1 | 0 | -4.626179 | -2.523239 | 1.283726 |
| 50 | 1 | 0 | -6.132687 | -4.320382 | 1.412405 |
| 51 | 1 | 0 | -5.668814 | -6.445869 | 0.293008 |
| 52 | 1 | 0 | -3.618608 | -6.664329 | -1.024491 |
| 53 | 1 | 0 | -2.126926 | -4.862228 | -1.263448 |
| 54 | 1 | 0 | -5.220215 | 2.852087 | -0.075554 |
| 55 | 1 | 0 | -4.510355 | 5.258834 | 1.446545 |
| 56 | 1 | 0 | 3.334676 | -4.283175 | -0.709889 |
| 57 | 1 | 0 | 4.946704 | -2.769253 | -1.146502 |
| 58 | 1 | 0 | 2.347709 | 0.245258 | -0.208168 |
| 59 | 1 | 0 | 2.369880 | -1.116549 | 1.001289 |
| 60 | 1 | 0 | 5.986793 | -0.846869 | -1.206968 |
| 61 | 1 | 0 | 4.967669 | 2.216324 | 1.539975 |
| 62 | 1 | 0 | 3.851231 | 2.244846 | 0.132321 |
| 63 | 1 | 0 | 1.810409 | 1.902162 | 1.533851 |
| 64 | 1 | 0 | 1.757885 | 0.602642 | 2.768249 |
| 65 | 1 | 0 | 2.831337 | 2.024774 | 3.005462 |
| 66 | 1 | 0 | 3.748333 | -0.964846 | 3.093630 |
| 67 | 1 | 0 | 4.812189 | 0.458633 | 3.346357 |
| 68 | 1 | 0 | 5.240415 | -0.775145 | 2.121734 |
| 69 | 1 | 0 | -3.349768 | 5.684726 | -2.470850 |
| 70 | 1 | 0 | -3.073722 | 4.188264 | -1.600975 |

**Table S5** The corresponding DFT coordinates for the optimized structures of **Lo-*cis***

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -3.224789 | -1.922790 | -0.102158 |
| 2 | 6 | 0 | -1.975081 | -2.468174 | -0.056809 |
| 3 | 6 | 0 | -4.338317 | -2.716356 | -0.070382 |
| 4 | 6 | 0 | -3.322537 | -0.561244 | -0.158877 |
| 5 | 6 | 0 | -4.366963 | 0.111406 | -0.775956 |
| 6 | 6 | 0 | -4.431666 | 1.480949 | -0.833916 |
| 7 | 6 | 0 | -3.454005 | 2.276824 | -0.270598 |
| 8 | 6 | 0 | -2.409651 | 1.626000 | 0.358893 |
| 9 | 6 | 0 | -2.352469 | 0.258637 | 0.406328 |
| 10 | 6 | 0 | -1.664485 | -3.645915 | 0.607576 |
| 11 | 6 | 0 | -0.382727 | -4.128403 | 0.686608 |
| 12 | 6 | 0 | 0.692717 | -3.461084 | 0.121227 |
| 13 | 6 | 0 | 0.370609 | -2.352274 | -0.642403 |
| 14 | 6 | 0 | -0.906162 | -1.866405 | -0.709482 |
| 15 | 6 | 0 | -5.545003 | -2.292875 | 0.469011 |
| 16 | 6 | 0 | -6.664125 | -3.089436 | 0.501850 |
| 17 | 6 | 0 | -6.630015 | -4.363283 | -0.010646 |
| 18 | 6 | 0 | -5.451516 | -4.815431 | -0.552289 |
| 19 | 6 | 0 | -4.339841 | -4.008516 | -0.577417 |
| 20 | 6 | 0 | -3.518759 | 3.673962 | -0.346444 |
| 21 | 7 | 0 | -2.636487 | 4.451291 | 0.170217 |
| 22 | 7 | 0 | -2.777617 | 5.801378 | 0.041061 |
| 23 | 6 | 0 | 1.996589 | -3.948118 | 0.276116 |
| 24 | 6 | 0 | 3.221711 | -3.369058 | 0.100975 |
| 25 | 6 | 0 | 3.641496 | -2.038370 | -0.011034 |
| 26 | 6 | 0 | 2.708573 | -0.850715 | 0.143210 |
| 27 | 6 | 0 | 4.978036 | -1.787790 | -0.192590 |
| 28 | 6 | 0 | 5.550716 | -0.522445 | -0.241918 |
| 29 | 6 | 0 | 4.660820 | 0.694205 | -0.067748 |
| 30 | 6 | 0 | 3.392770 | 0.392842 | 0.763227 |
| 31 | 6 | 0 | 6.903156 | -0.355138 | -0.452733 |
| 32 | 6 | 0 | 2.427553 | 1.594145 | 0.685230 |
| 33 | 6 | 0 | 3.755608 | 0.141404 | 2.242330 |
| 34 | 6 | 0 | -1.702652 | 6.664433 | 0.011665 |
| 35 | 7 | 0 | -2.052536 | 7.991387 | 0.018965 |

| | | | | | |
|---|---|---|---|---|---|
| 36 | 16 | 0 | -0.130752 | 6.189798 | -0.045258 |
| 37 | 6 | 0 | 7.465799 | 0.899224 | -0.508487 |
| 38 | 7 | 0 | 7.943393 | 1.968513 | -0.558979 |
| 39 | 6 | 0 | 7.761285 | -1.415948 | -0.629438 |
| 40 | 7 | 0 | 8.497175 | -2.315925 | -0.777883 |
| 41 | 1 | 0 | -5.154479 | -0.433846 | -1.302227 |
| 42 | 1 | 0 | -5.273223 | 1.941709 | -1.361681 |
| 43 | 1 | 0 | -1.612994 | 2.198505 | 0.840730 |
| 44 | 1 | 0 | -1.512505 | -0.160355 | 0.967657 |
| 45 | 1 | 0 | -2.425589 | -4.193979 | 1.168751 |
| 46 | 1 | 0 | -0.211146 | -5.037525 | 1.272289 |
| 47 | 1 | 0 | 1.135919 | -1.867396 | -1.249285 |
| 48 | 1 | 0 | -1.062010 | -0.997120 | -1.355615 |
| 49 | 1 | 0 | -5.640814 | -1.317688 | 0.952587 |
| 50 | 1 | 0 | -7.584476 | -2.711364 | 0.956073 |
| 51 | 1 | 0 | -7.517452 | -5.000941 | 0.012858 |
| 52 | 1 | 0 | -5.401087 | -5.819867 | -0.982160 |
| 53 | 1 | 0 | -3.461169 | -4.422775 | -1.078431 |
| 54 | 1 | 0 | -4.371897 | 4.135609 | -0.871242 |
| 55 | 1 | 0 | -3.713845 | 6.194191 | 0.013388 |
| 56 | 1 | 0 | 2.049334 | -5.000897 | 0.590291 |
| 57 | 1 | 0 | 4.042224 | -4.099677 | 0.142737 |
| 58 | 1 | 0 | 2.349872 | -0.551261 | -0.860311 |
| 59 | 1 | 0 | 1.839528 | -1.113981 | 0.769930 |
| 60 | 1 | 0 | 5.645711 | -2.649143 | -0.301050 |
| 61 | 1 | 0 | 5.208124 | 1.525635 | 0.410407 |
| 62 | 1 | 0 | 4.368564 | 1.043404 | -1.078246 |
| 63 | 1 | 0 | 2.133887 | 1.816053 | -0.356767 |
| 64 | 1 | 0 | 1.501747 | 1.398245 | 1.255607 |
| 65 | 1 | 0 | 2.892307 | 2.505647 | 1.100784 |
| 66 | 1 | 0 | 2.850554 | -0.076970 | 2.837151 |
| 67 | 1 | 0 | 4.239021 | 1.030214 | 2.685729 |
| 68 | 1 | 0 | 4.447661 | -0.708646 | 2.366632 |
| 69 | 1 | 0 | -1.324736 | 8.688033 | -0.010385 |
| 70 | 1 | 0 | -3.017763 | 8.290105 | 0.058900 |