Electronic Supplementary Material (ESI) for Dalton Transactions
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# Metal(II) complexes based on 1,4-bis(3-pyridylaminomethyl)benzene: Structures, photoluminescence and photocatalytic properties

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**Table S1** Selected bond lengths (Å) and angles (º) for complexes **1-4**

| | | | |
|---|---|---|---|
| ***Complex 1*** | | | |
| Cd(1)-O(3) | 2.3085(17) | Cd(1)-O(1) | 2.3361(15) |
| Cd(1)-N(1) | 2.3178(19) | Cd(1)-N(1)#1 | 2.3178(19) |
| O(3)#1-Cd(1)-O(3) | 180.00(8) | O(3)-Cd(1)-O(1)#1 | 81.53(6) |
| O(3)-Cd(1)-N(1)#1 | 88.74(7) | O(3)-Cd(1)-N(1) | 91.26(7) |
| N(1)-Cd(1)-O(1) | 89.83(6) | N(1)#1-Cd(1)-N(1) | 180.00(8) |
| ***Complex 2*** | | | |
| Cd(1)-O(2)#2 | 2.261(2) | Cd(1)-O(4)#4 | 2.453(3) |
| Cd(1)-N(4)#3 | 2.302(3) | Cd(1)-N(1) | 2.370(3) |
| O(3)#4-Cd(1)-O(4)#4 | 55.01(8) | O(2)#2-Cd(1)-O(3)#4 | 139.57(9) |
| N(4)#3-Cd(1)-O(1) | 87.74(9) | O(1)-Cd(1)-N(1) | 173.88(8) |
| O(2)#2-Cd(1)-N(1) | 89.25(9) | N(4)#3-Cd(1)-N(1) | 86.69(10) |

| | | | |
|---|---|---|---|
| ***Complex 3*** | | | |
| Pb(1)-O(1) | 2.369(4) | Pb(1)-O(4)#5 | 2.718(4) |
| Pb(1)-O(2) | 2.607(5) | Pb(1)-N(2) | 2.620(4) |
| O(3)#5-Pb(1)-O(4)#5 | 50.07(13) | O(2)-Pb(1)-O(4)#5 | 178.71(13) |
| O(1)-Pb(1)-N(2)#6 | 81.39(8) | N(2)-Pb(1)-O(4)#5 | 92.07(9) |
| O(3)#5-Pb(1)-N(2) | 84.31(8) | N(2)#6-Pb(1)-N(2) | 161.16(16) |
| ***Complex 4*** | | | |
| Zn(1)-O(2)#7 | 2.0335(14) | Zn(1)-O(4)#9 | 2.1029(14) |
| Zn(1)-O(1) | 2.0393(15) | Zn(1)-N(1) | 2.0158(16) |
| O(1)-Zn(1)-O(3)#8 | 86.71(6) | O(3)#8-Zn(1)-O(4)#9 | 157.93(6) |
| O(2)#7-Zn(1)-O(1) | 157.20(6) | N(1)-Zn(1)-O(3)#8 | 99.28(6) |
| N(1)-Zn(1)-O(1) | 102.02(7) | N(1)-Zn(1)-O(2)#7 | 100.67(6) |

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 -x+2,-y+1,-z+1 #3 -x+1,-y+2,-z+1 #4 -x+1,-y+1,-z+1
#5 x, y, z-1 #6 x,-y+1/2,z #7 -x+1/2,-y+1/2,-z+1 #8 x,-y,z-1/2
#9 -x+1/2,y+1/2,-z+3/2

**Table S2** Distances (Å) and angles (°) of the selected H bonds in complexes **1-4**

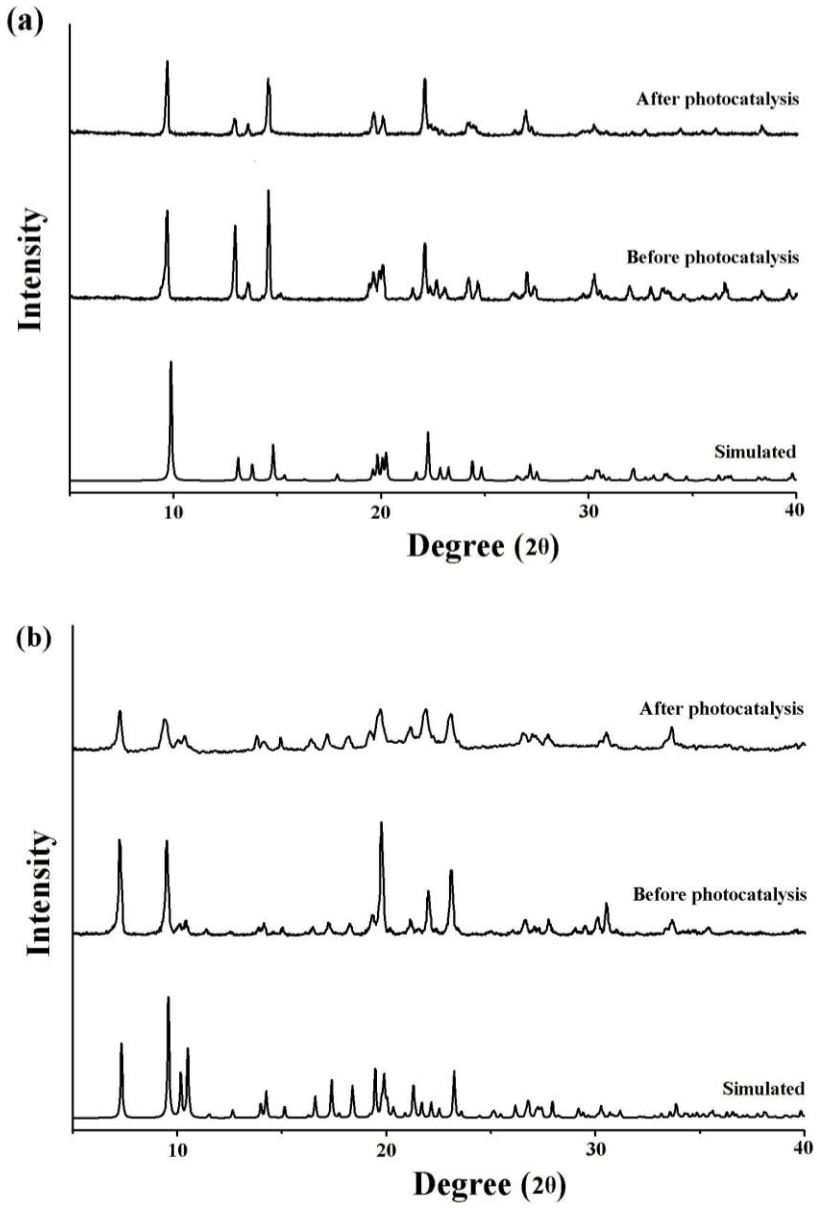
| *D* | *H* | *A* | *D–H* | *D···A distance* | *H···A distance* | *∠D–H···A* |
|---|---|---|---|---|---|---|
| *Complex **1*** | | | | | | |
| N2 | H2B | O2#1 | 0.90 | 2.995 | 2.264 | 138 |
| O3 | H3B | S1#2 | 0.85 | 3.389 | 2.853 | 123 |
| O3 | H3B | O2#3 | 0.85 | 2.722 | 1.956 | 149 |
| O3 | H3C | N2#4 | 0.85 | 2.813 | 1.994 | 162 |
| *Complex **2*** | | | | | | |
| N2 | H2 | O2#5 | 0.86 | 3.034 | 2.425 | 128 |
| N3 | H3 | O4#6 | 0.86 | 2.945 | 2.097 | 169 |

| | | | | | | |
|---|---|---|---|---|---|---|
| *Complex **3*** | | | | | | |
| N1 | H1 | O3#7 | 0.86 | 3.147 | 2.402 | 145 |
| *Complex **4*** | | | | | | |
| N2 | H2 | O3#8 | 0.86 | 3.182 | 2.496 | 137 |

Symmetry transformations used to generate the equivalent atoms:

#1: x+1/2, y-1/2, z; #2: -x, -y+1, -z+1; #3: x, -y+1, z+1/2; #4: -x, y, -z+1/2; #5: x, y, z-1;

#6: -x, -y+2, -z+1; #7: -x+1, -y, -z+2; #8: -x+1, y+1, -z+3/2



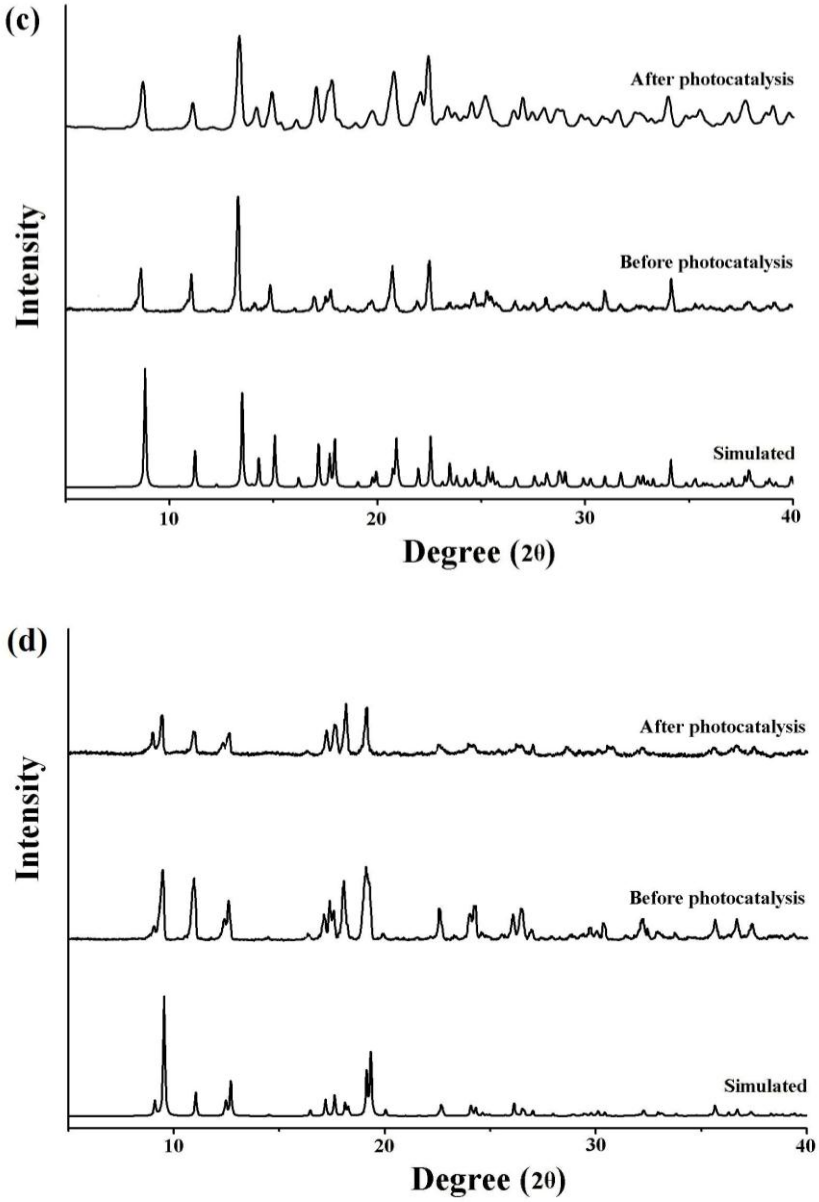



**Fig.S1** The PXRD patterns of complexes **1** (**a**), **2** (**b**), **3** (**c**) and **4** (**d**).

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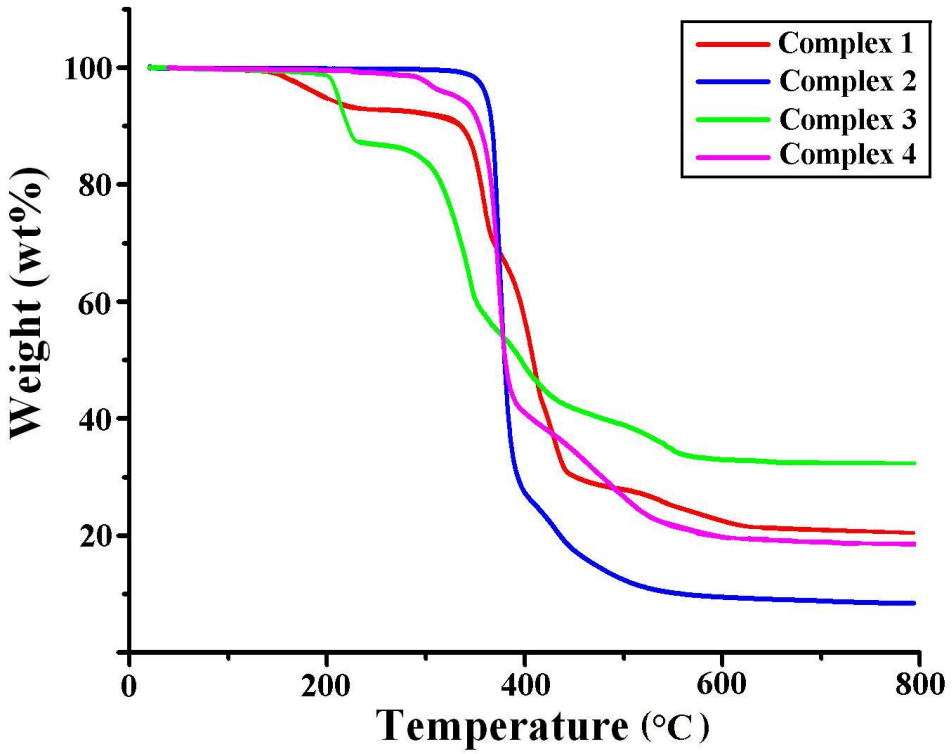
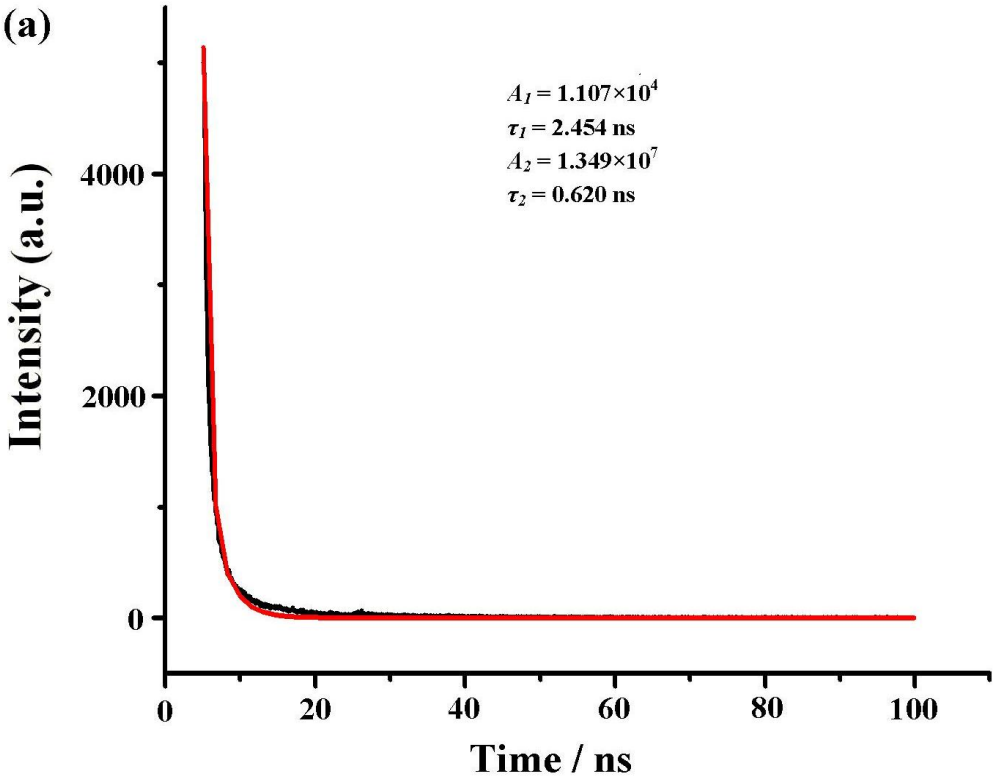
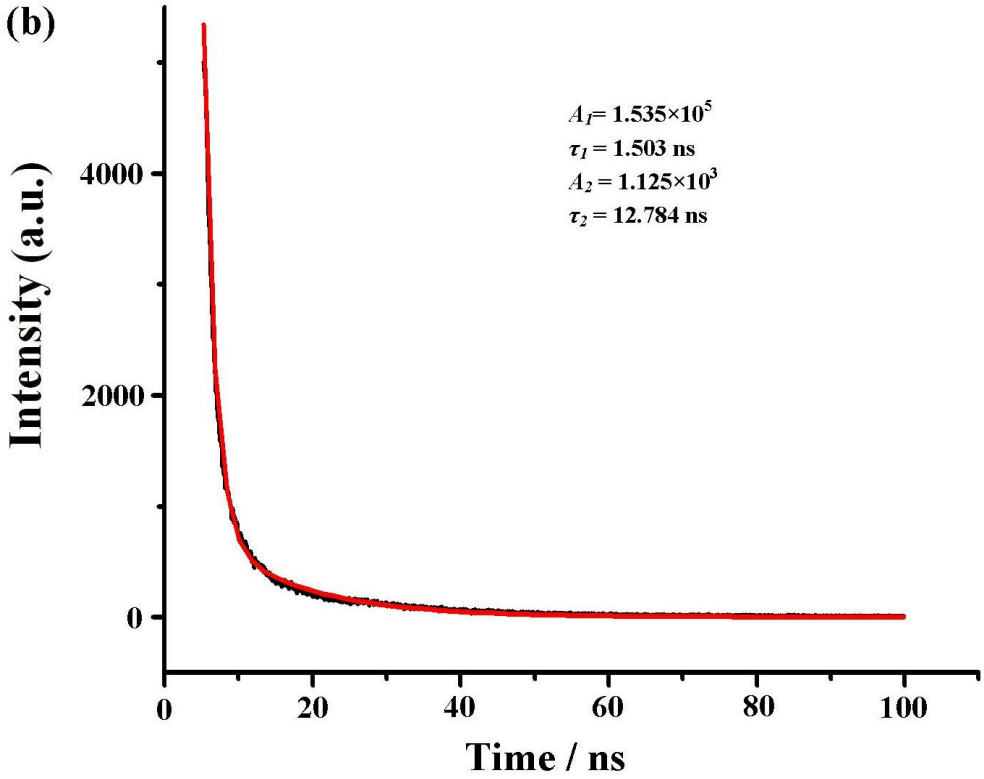
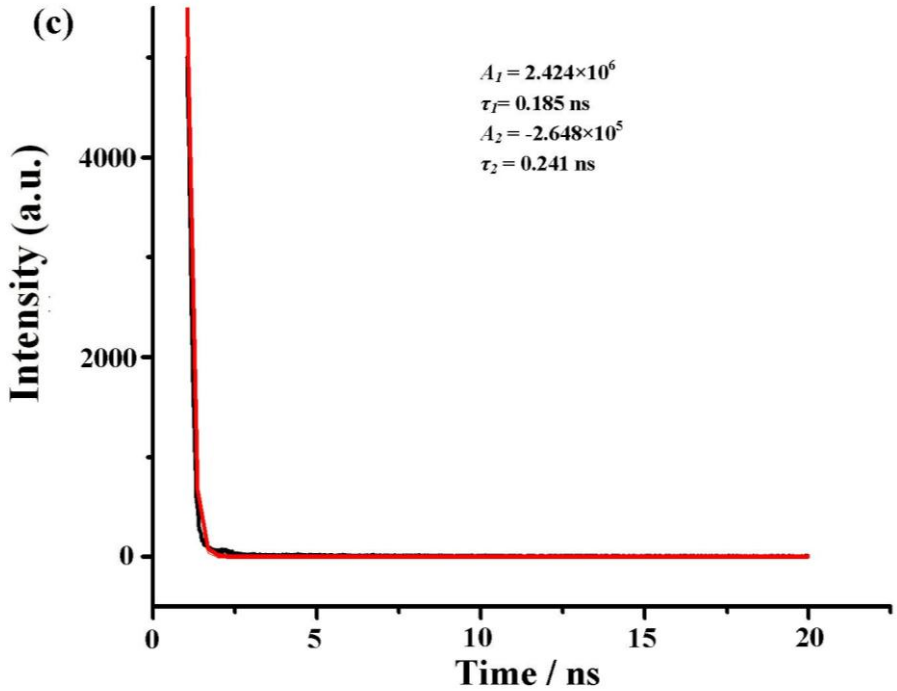



**Fig. S2** Thermogravimetric curves of complexes **1** (**red**), **2**(**blue**), **3**(**green**) and **4** (**pink**).


(a)
$A_1$ = 1.107×10$^4$
$\tau_1$ = 2.454 ns
$A_2$ = 1.349×10$^7$
$\tau_2$ = 0.620 ns
Intensity (a.u.)
0
2000
4000
0
20
40
60
80
100
Time / ns


(b)
$A_1$= 1.535×10$^5$
$\tau_1$ = 1.503 ns
$A_2$ = 1.125×10$^3$
$\tau_2$ = 12.784 ns
Intensity (a.u.)
0
2000
4000
0
20
40
60
80
100
Time / ns



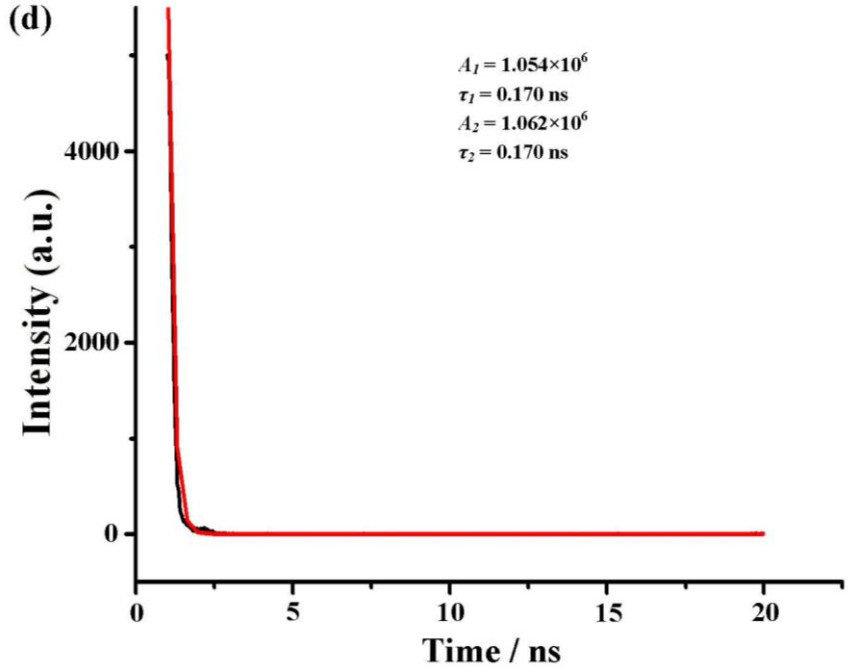




**Fig. S3** Typical luminescence decay profile observed in the solid state at room temperature (black lines) and the corresponding biexponential fits (red lines) for complexes **1** (**a**), **2** (**b**), **3** (**c**) and **4** (**d**).

The equation $I_t = A_1 \times \exp(-t/\tau_1) + A_2 \times \exp(-t/\tau_2)$ was utilized for fitting the fluorescence decay curves, which gave the best parameters as follows:

$A_1 = 1.107\times10^4$, $\tau_1 = 2.454$ ns, $A_2 = 1.349\times10^7$ and $\tau_2 = 0.620$ ns with an overall $\chi^2$ of 0.9920 for complex **1**,

$A_1 = 1.535\times10^5$, $\tau_1 = 1.503$ ns, $A_2 = 1.125\times10^3$ and $\tau_2 = 12.784$ ns with an overall $\chi^2$ of 0.9973 for complex **2**,

$A_1 = 2.424\times10^6$, $\tau_1 = 0.185$ ns, $A_2 = -2.648\times10^5$ and $\tau_2 = 0.241$ ns with an overall $\chi^2$ of 0.9908 for complex **3**,

$A_1 = 1.054\times10^6$, $\tau_1 = 0.170$ ns, $A_2 = 1.062\times10^6$ and $\tau_2 = 0.170$ ns with an overall $\chi^2$ of 0.9780 for complex **4**.

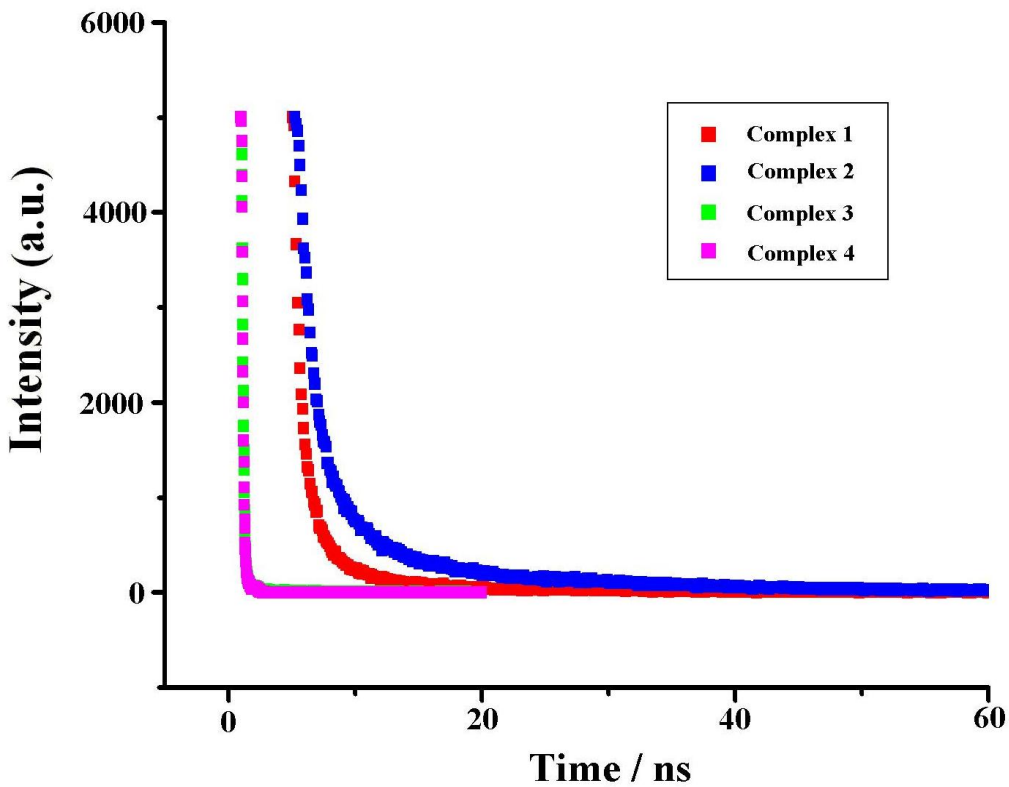



**Fig. S4** Room temperature emission decay curves for complexes **1** (**red**), **2** (**blue**), **3** (**green**) and **4** (**pink**).

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The formula for the calculation of band gap is as follows:

Band Gap energy = $hc/\lambda = 1240/\lambda$ eV

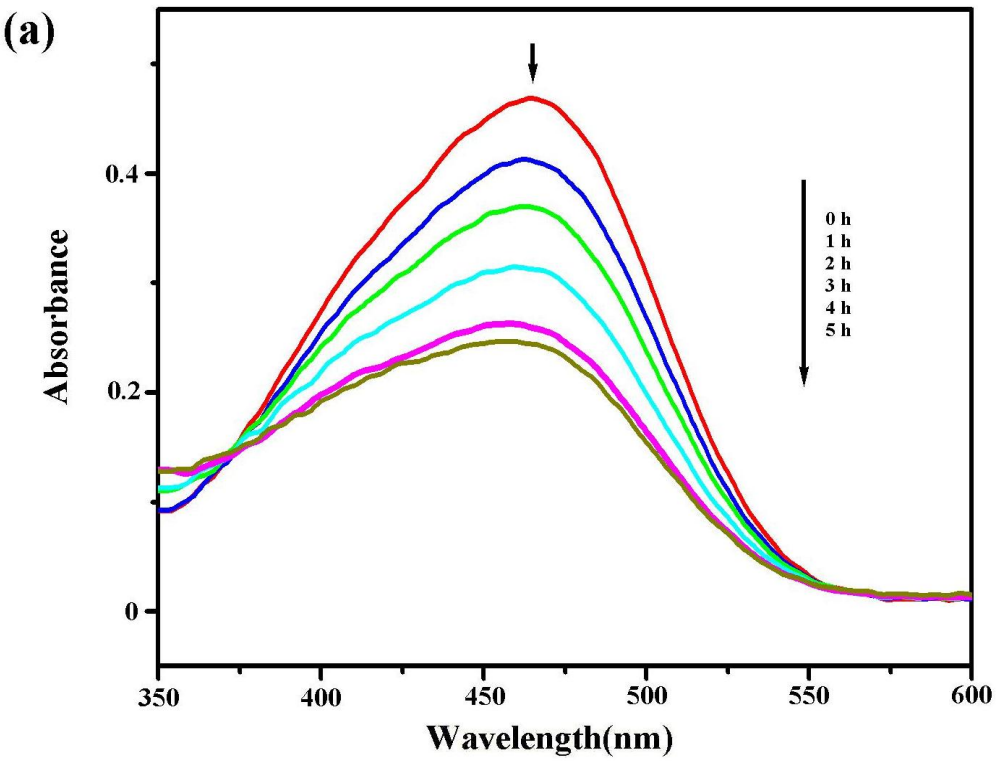
h = planks constant = $6.626 \times 10^{-34}$ Joules ·sec

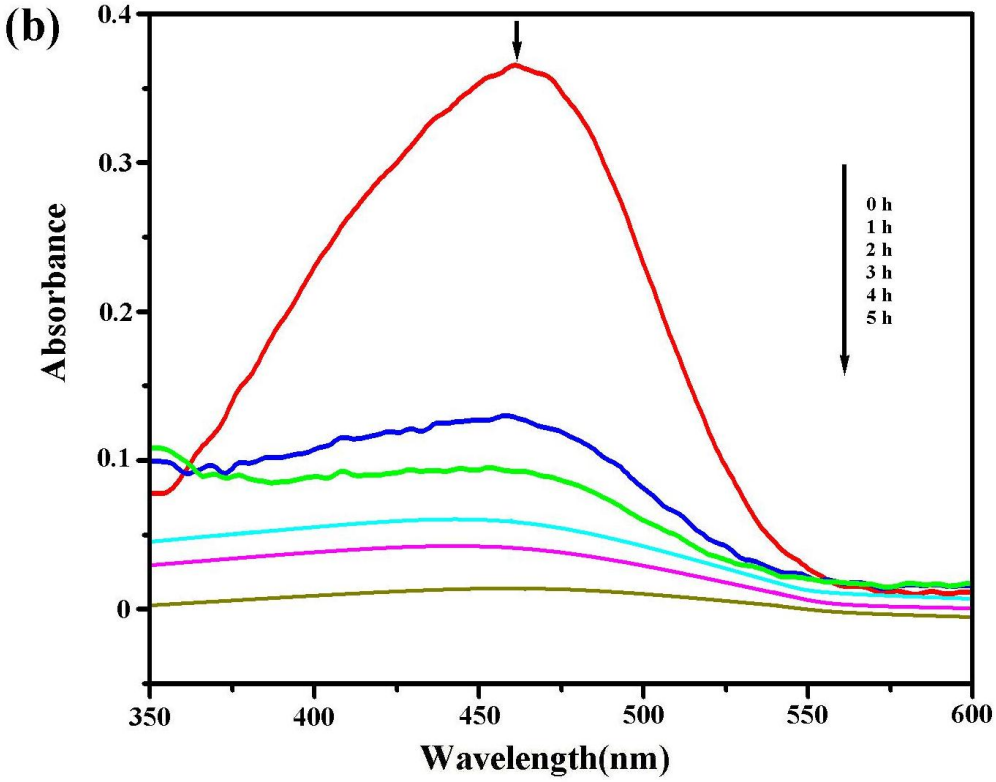
c = Speed of light = $3.0 \times 10^{8}$ meter/sec

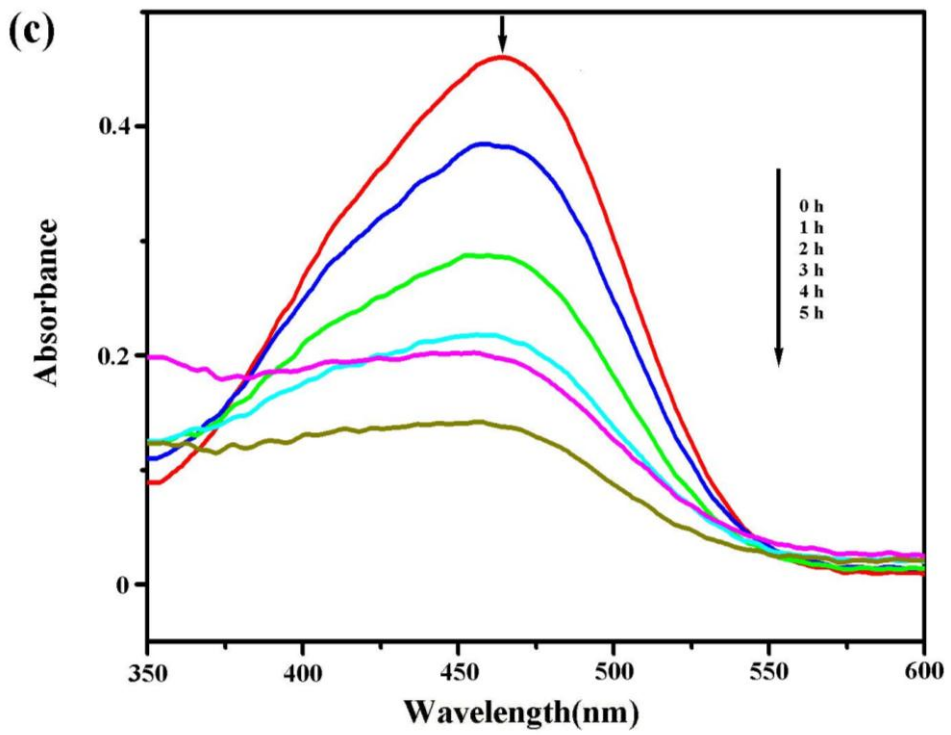
$\lambda$ = cut off wavelength (nm)

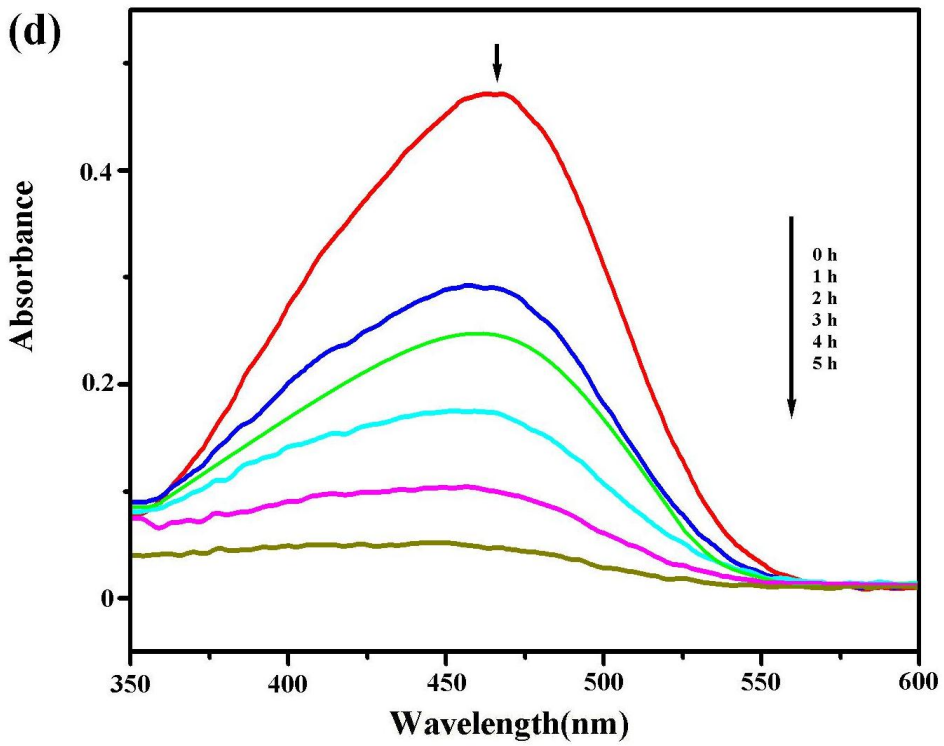
where 1eV = $1.6 \times 10^{-19}$ Joules (conversion factor)

$\lambda$, the cut off wavelength, is obtained according to the diffuse reflectance spectrum {F(R) vs. wavelength, $F(R) = (1-R)^2/2R$, R is the experimentally observed reflectance}.


(a)
Absorbance
0.4
0.2
0
350
400
450
500
550
600
Wavelength(nm)
0 h
1 h
2 h
3 h
4 h
5 h


(b)
Absorbance
0.4
0.3
0.2
0.1
0
350
400
450
500
550
600
Wavelength(nm)
0 h
1 h
2 h
3 h
4 h
5 h


(c)
Absorbance
0.4
0.2
0
350
400
450
500
550
600
Wavelength(nm)
0 h
1 h
2 h
3 h
4 h
5 h


(d)
Absorbance
0.4
0.2
0
350
400
450
500
550
600
Wavelength(nm)
0 h
1 h
2 h
3 h
4 h
5 h

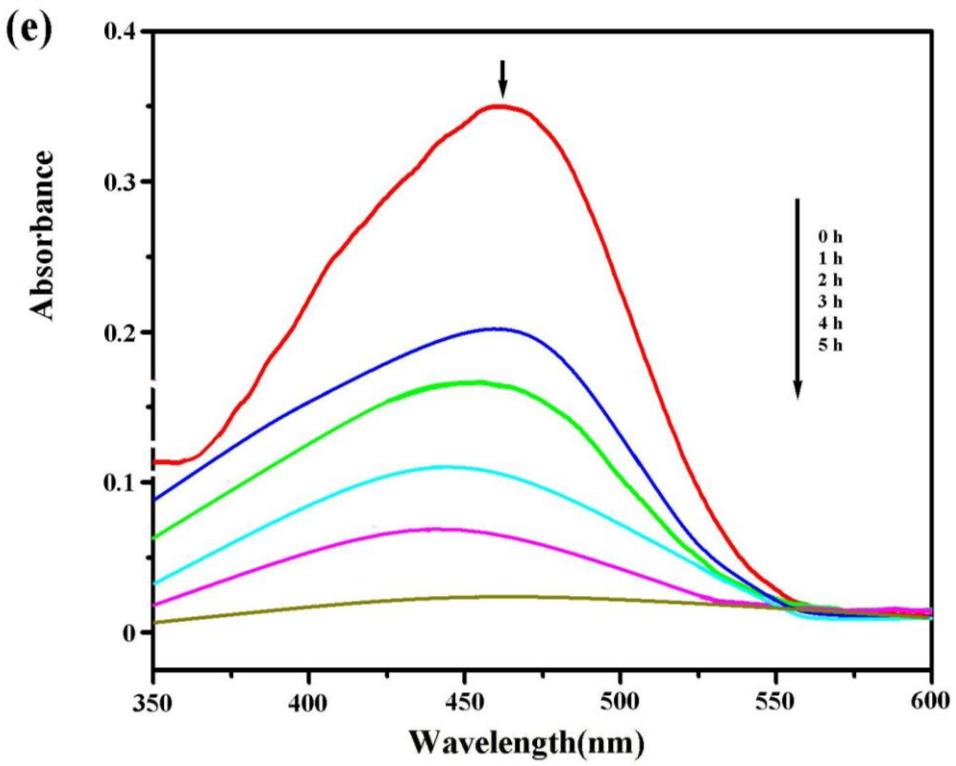



**Fig. S5** UV-visible spectral changes of MO in the absence (**a**) and presence of catalysts: complexes **1** (**b**), **2** (**c**), **3** (**d**) and **4** (**e**).