Supplementary material:

Triphenylethylene-based biimidazoles showing preferable detection of explosives and their rhenium complexes undergoing chiral and *cis-trans* transformations

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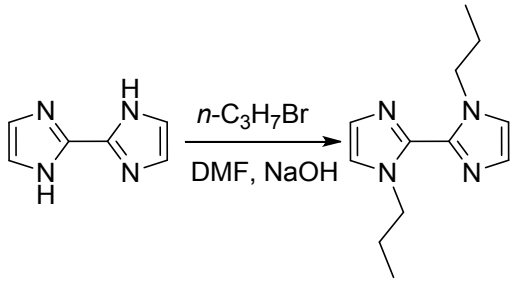
1. General

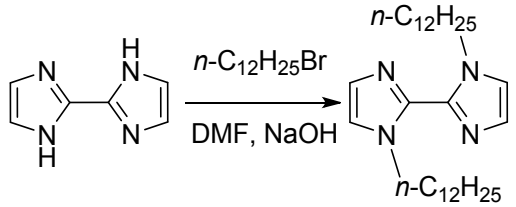
The reagents of analytical grade were purchased from commercial sources and used without any further purification. Caution: All explosives or explosive precursors should be handled only in small quantities. Infrared (IR) spectra (4000–400 cm^{-1}) were recorded using a Nicolet FT–IR 170X spectrophotometer on KBr disks. ^1H NMR spectra were measured with a Bruker DMX 500 MHz NMR spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as the internal reference. UV–Vis spectra were recorded with a Shimadzu UV–3600 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm. Luminescence spectra were recorded on Fluorescence spectrophotometer at room temperature (25°C) using the

same solution as those for the UV–Vis determination. The crystal system was determined by Laue symmetry, and the space groups were assigned on the basis of systematic absences using XPREP. Absorption correction was performed on the data, and the structures were solved by direct methods and refined by full-matrix least-squares methods on Fo^2 by using the SHELXTL-PC software package. All non-H atoms were anisotropically refined, and all hydrogen atoms were inserted in calculated positions, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent atoms.

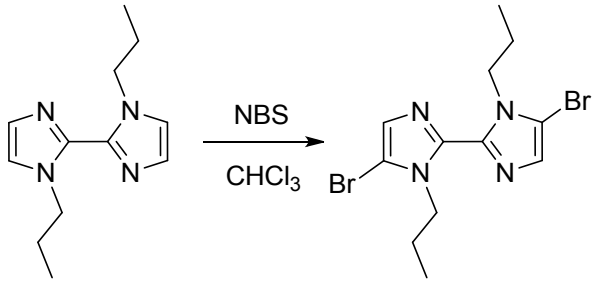
2. Synthetic details



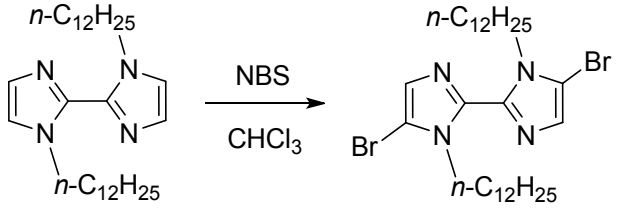
1,1'-dipropyl-1*H*,1'*H*-2,2'-biimidazole (**1a**): In a 100 mL flask, 2,2'-biimidazole (1.00 g, 7.45 mmol), 30 mL DMF and NaOH (0.65 g, 16.40 mmol) were added. After stirring for half an hour at room temperature, 1-bromopropane (2.29 g, 18.63 mmol) was added slowly. The mixture was stirred at room temperature. Five hours later, the reaction product was dissolved in H_2O (45 mL) and extracted with dichloromethane (3 × 45 mL). The solvent was evaporated and purified by column chromatogram. Finally, the pure product (1.38 g, 85%) was afforded. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (s, 2H, imidazole), 6.99 (s, 2H, imidazole), 4.40 (t, 4H, NCH_2), 1.81-1.72 (m, 4H, CH_2), 0.87 (t, 6H, CH_3).



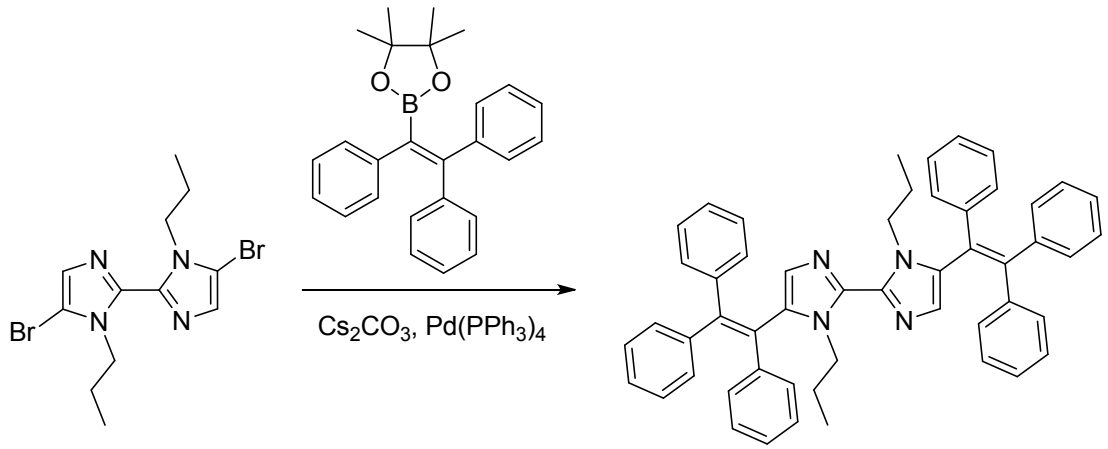
1,1'-didodecyl-1*H*,1'*H*-2,2'-biimidazole (**2a**): The procedure for the synthesis of compound **1a** was repeated except that 1-bromododecane (4.64 g, 18.63 mmol) was used instead of 1-bromopropane (2.29 g, 18.63 mmol). Yield: 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (s, 2H, imidazole), 6.98 (s, 2H, imidazole), 4.41 (t, 4H, NCH_2), 1.73-1.69 (m, 4H, CH_2), 1.24-1.22 (m, 36H, CH_2), 0.87 (t, 6H, CH_3).



5,5'-dibromo-1,1'-dipropyl-1*H*,1'*H*-2,2'-biimidazole (**1b**): Compound **1a** (0.30 g, 1.37 mmol) was dissolved in 10 mL chloroform, and then *N*-bromosuccinimide (2.3 equivalents) was added drop by drop for 1 hour at 0 ^{o}C. Two hours later, the mixture was extracted with water and dichloromethane and purified by column chromatogram. The yellow solid (0.43 g, 83%) was achieved. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (s, 2H, imidazole), 4.42 (t, 4H, NCH_2), 1.74-1.60 (m, 4H, CH_2), 0.87 (t, 6H, CH_3).

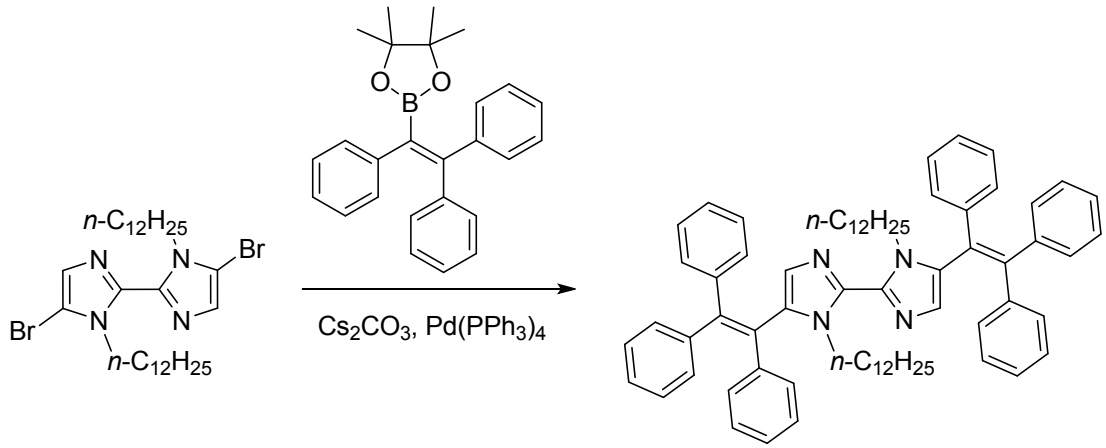


5,5'-dibromo-1,1'-didodecyl-1*H*,1'*H*-2,2'-biimidazole (**2b**): The procedure for the synthesis of compound **1b** was repeated except that compound **2a** (0.64 g, 1.37 mmol) was used instead of compound **1a** (0.30 g, 1.37 mmol). Yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (s, 2H, imidazole), 4.44 (t, 4H, NCH_2), 1.67-1.64 (m, 4H, CH_2), 1.25-1.24 (m, 36H, CH_2), 0.88 (t, 6H, CH_3).

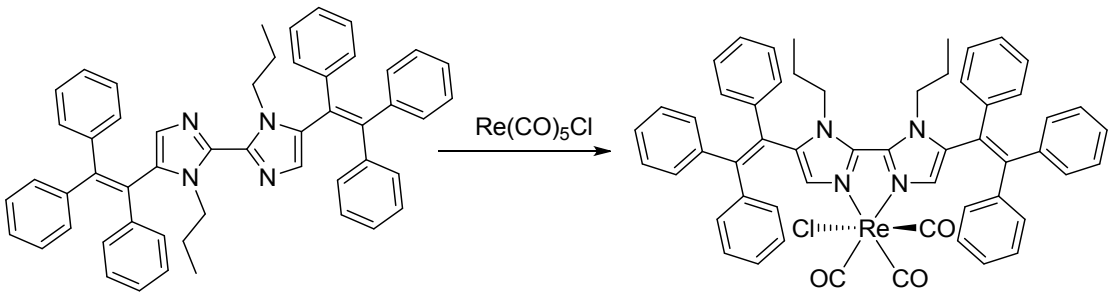


1,1'-dipropyl-5,5'-bis(1,2,2-triphenylvinyl)-1*H*,1'*H*-2,2'-biimidazole (**1**): In a 50

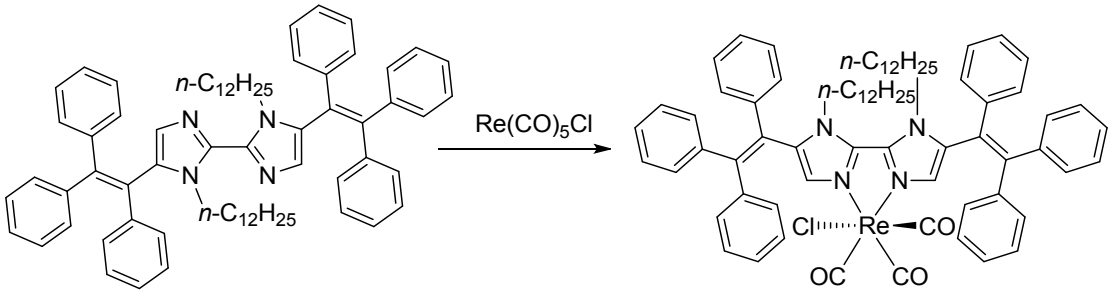
mL flask, compound **1b** (0.10 g, 0.26 mmol), 4,4,5,5-tetramethyl-2-(1,2,2-triphenylvinyl)-1,3,2-dioxaborolane (TPE-Bpin, 0.22 g, 0.58 mmol), Cs_2CO_3 (0.22 g, 0.66 mmol,) and $Pd(PPh_3)_4$ (30.7 mg, 0.026 mmol,) was mixed with degassed, and then 2 mL H_2O and 10 mL dioxane were added in the mixture. The mixture was heated at 95 °C for 24 h under argon atmosphere. Then, water was added to quench the reaction until fully finishing of the reaction. The mixture was extracted with water and dichloromethane. Then, the solution was collected and evaporated. After being purified by column chromatogram and few times of re-crystallization, the target product was achieved with a yield of 78%. FT−IR (KBr pellets, cm^{-1}): 3429 (b), 3051 (m), 2962 (m), 2874 (w), 1595 (m), 1498 (m), 1434 (m), 1076 (m), 1032 (m), 939 (m), 750 (m), 698 (s). ^1H NMR (500 MHz, $CDCl_3$): δ 7.11-7.03 (m, 30H, benzene), 6.61 (s, 2H, imidazole), 3.75 (t, 4H, NCH_2), 1.28-1.26 (m, 4H, CH_2), 0.59 (t, 6H, CH_3). ESI−MS (m/z): calcd for $[C_{52}H_{46}N_4]$: 726.3722; $[C_{52}H_{46}N_4Na]^+$: 749.3620. Found: 749.3551.



1,1'-didodecyl-5,5'-bis(1,2,2-triphenylvinyl)-1*H*,1'*H*-2,2'-biimidazole (**2**): The procedure for the synthesis of compound **1** was repeated except that compound **2b** (0.16 g, 0.26 mmol) was used instead of compound **1b** (0.10 g, 0.26 mmol). Yield: 75%. FT−IR (KBr pellets, cm^{-1}): 3426 (b), 3079 (w), 3019 (m), 2926 (s), 2854 (m), 1599 (w), 1442 (m), 1362 (m), 1253 (m), 1076 (m), 1032 (m), 819 (m), 694 (s). ^1H NMR (500 MHz, $CDCl_3$): δ 7.11-7.03 (m, 18H+12H, benzene), 6.60 (s, 2H, imidazole), 3.83 (t, 4H, NCH_2), 1.26-1.24 (m, 28H, CH_2), 1.14 (m, 4H, CH_2), 0.93 (m, 4H, CH_2), 0.89-0.87 (m, 10H, CH_2CH_3). ESI−MS (m/z): calcd for $[C_{70}H_{82}N_4]$: 978.6539; $[C_{70}H_{82}N_4Na]^+$: 1001.6437. Found: 1001.6342.



[ReL(CO)$_3$Cl] (**Re1, L = 1**): A mixture of compound **1** (50.2 mg, 0.069 mmol) and $Re(CO)_5Cl$ (25.0 mg, 0.069 mmol) were dissolved in 25 mL CH_3Cl/CH_3CN (*v*/*v* = 1:1). After refluxing for 3 h, the solvent was removed, and the target complex was afforded with a yield of 75%. The single crystals have been grown from *n*-hexane and $CHCl_3$ (*v*/*v* = 1:1) through slow evaporation for 3 days at room temperature. FT−IR (KBr pellets, cm^{-1}): 3438 (b), 2922 (w), 2017 (m), 1905 (m), 1885 (m), 1635 (m), 1442 (m), 1257 (m), 1027 (w), 698 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22-7.00 (m, 30H+2H, benzene+imidazole), 3.26 (s, 4H, NCH_2), 1.28-1.25 (m, 4H, CH_2), 0.65 (t, 6H, CH_3).



[ReL(CO)$_3$Cl] (**Re2, L = 2**): The procedure for the synthesis of compound **Re1** was repeated except that compound **2** (67.6 mg, 0.069 mmol) was used instead of compound **1** (50.2 mg, 0.069 mmol). Yield: 71%. FT−IR (KBr pellets, cm^{-1}): 3431 (b), 2960 (w), 2926 (m), 2853 (w), 2016 (m), 1912 (m), 1815 (m), 1265 (m), 1100 (m), 1024 (m), 799 (m), 690 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23-7.00 (m, 30H, benzene), 6.98 (s, 2H, imidazole), 3.25 (s, 4H, NCH_2), 1.43-1.41 (m, 4H, CH_2), 1.26-1.15 (m, 32H, CH_2), 0.99-0.93 (m, 4H, CH_2), 0.89-0.86 (m, 6H, CH_3). ESI−MS (m/z): calcd for $[C_{73}H_{82}ClN_4O_3Re]$: 1284.5633; $[C_{73}H_{82}N_4O_3Re]^+$: 1249.5944. Found: 1249.5740.

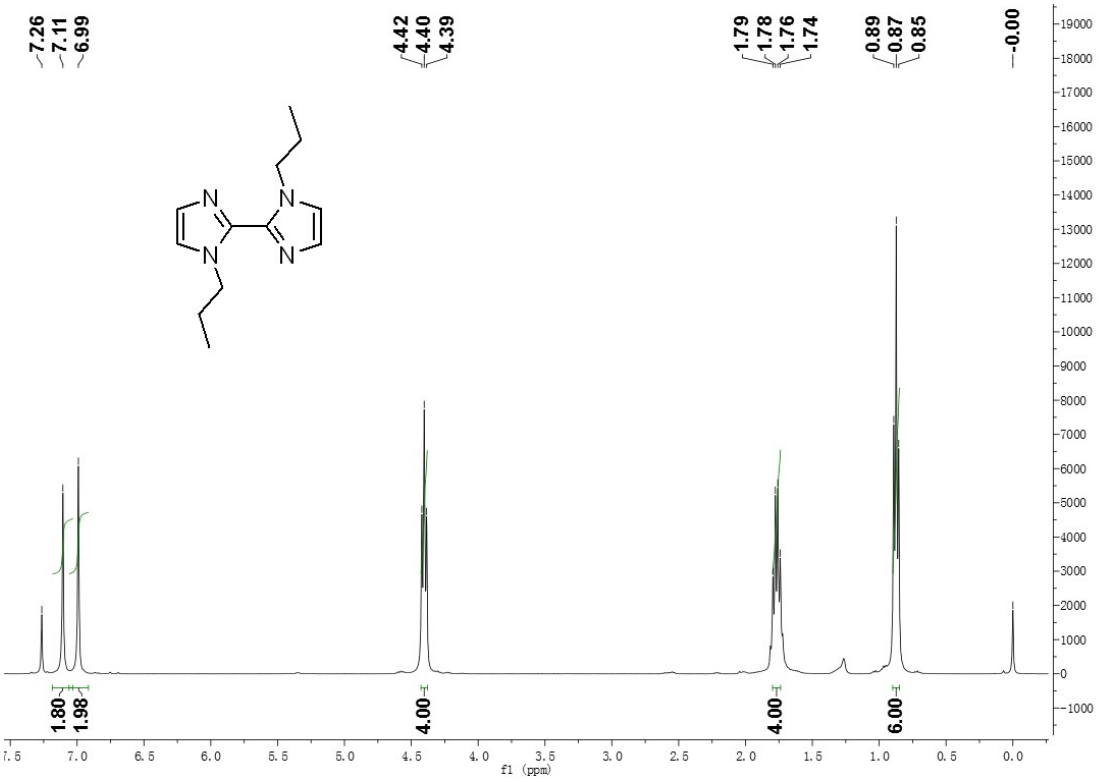


Fig. S1. ^{1}H NMR of compound **1a**.

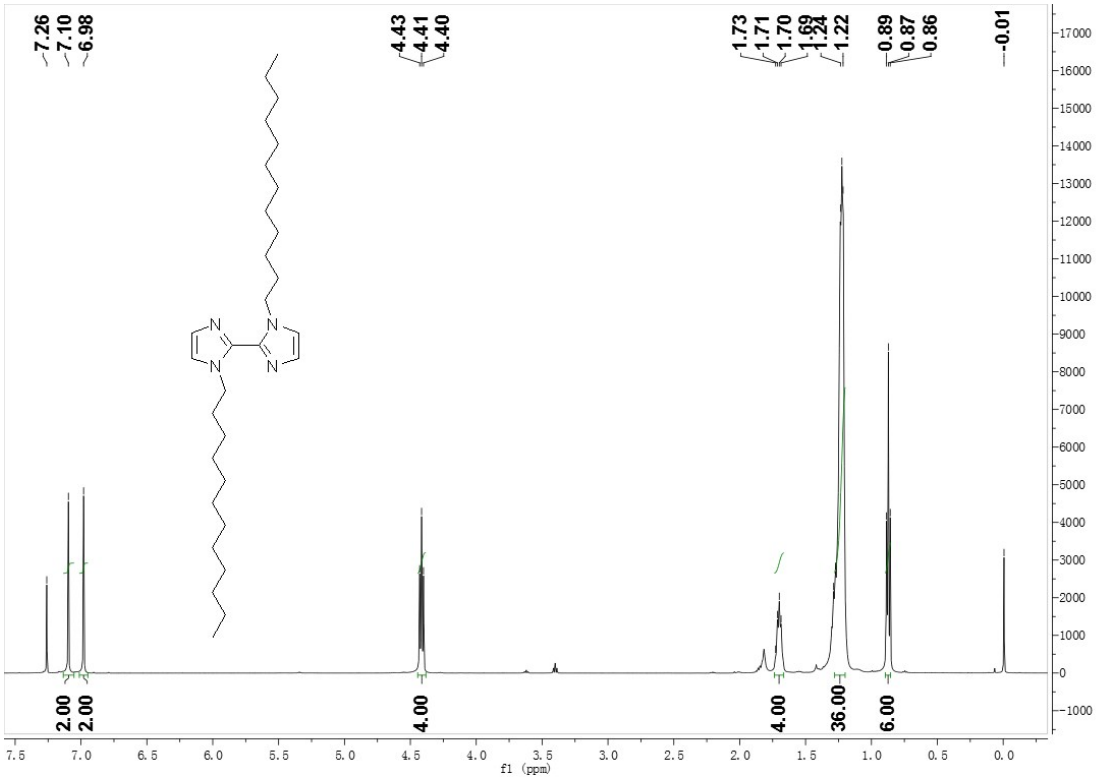


Fig. S2. ^{1}H NMR of compound **2a**.

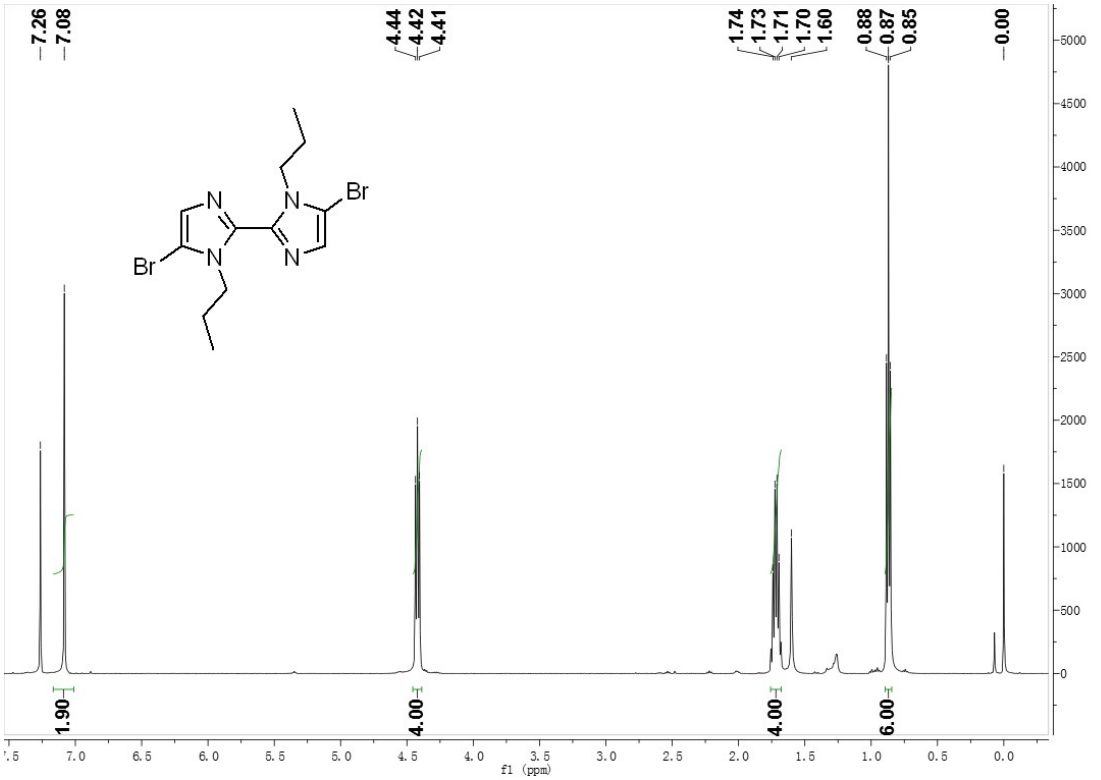


Fig. S3. ^{1}H NMR of compound **1b**.

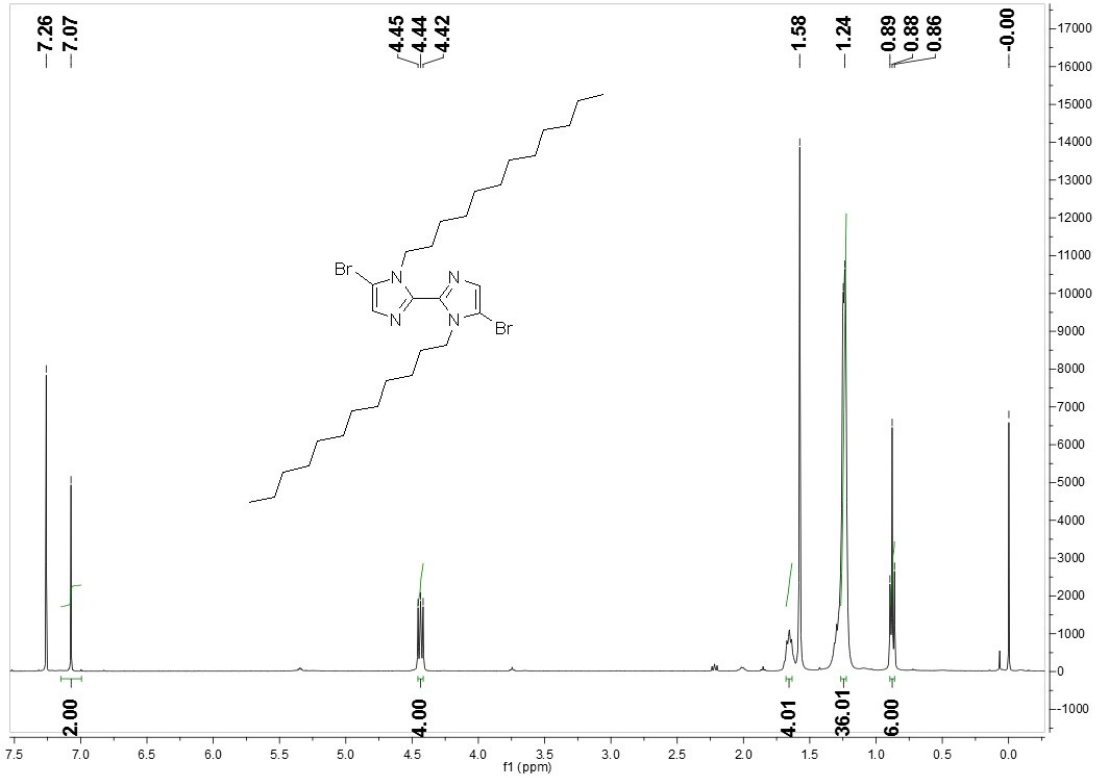
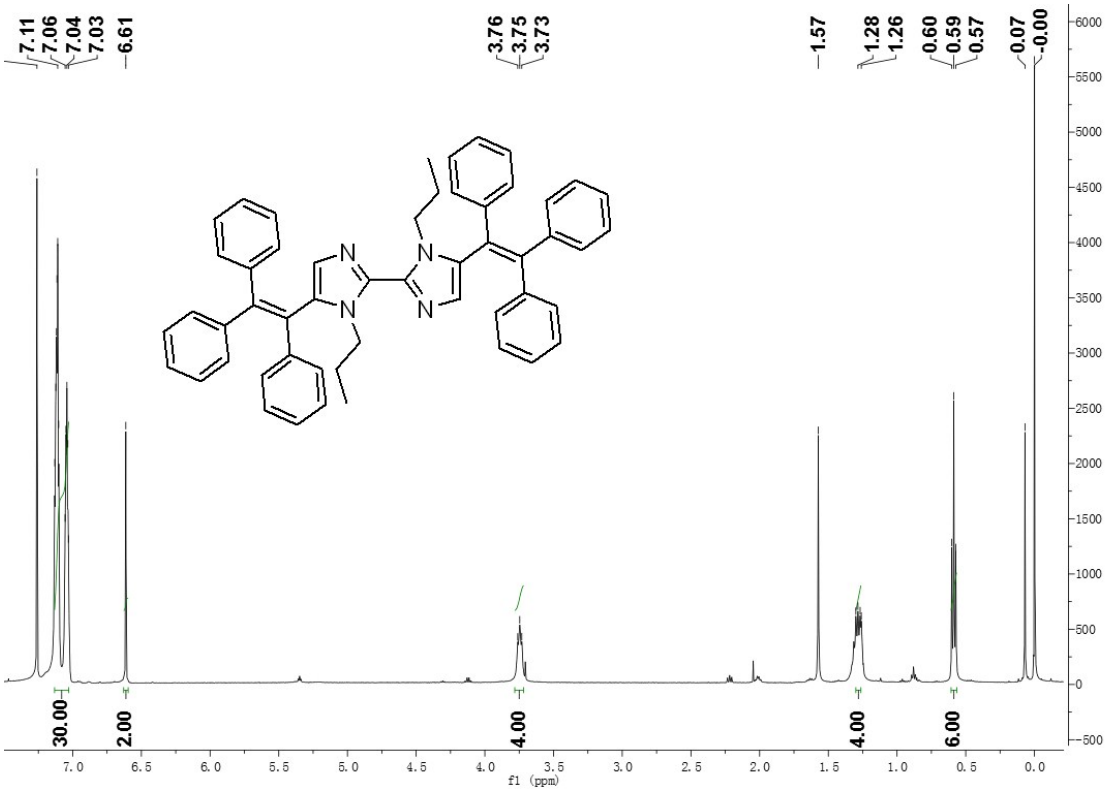
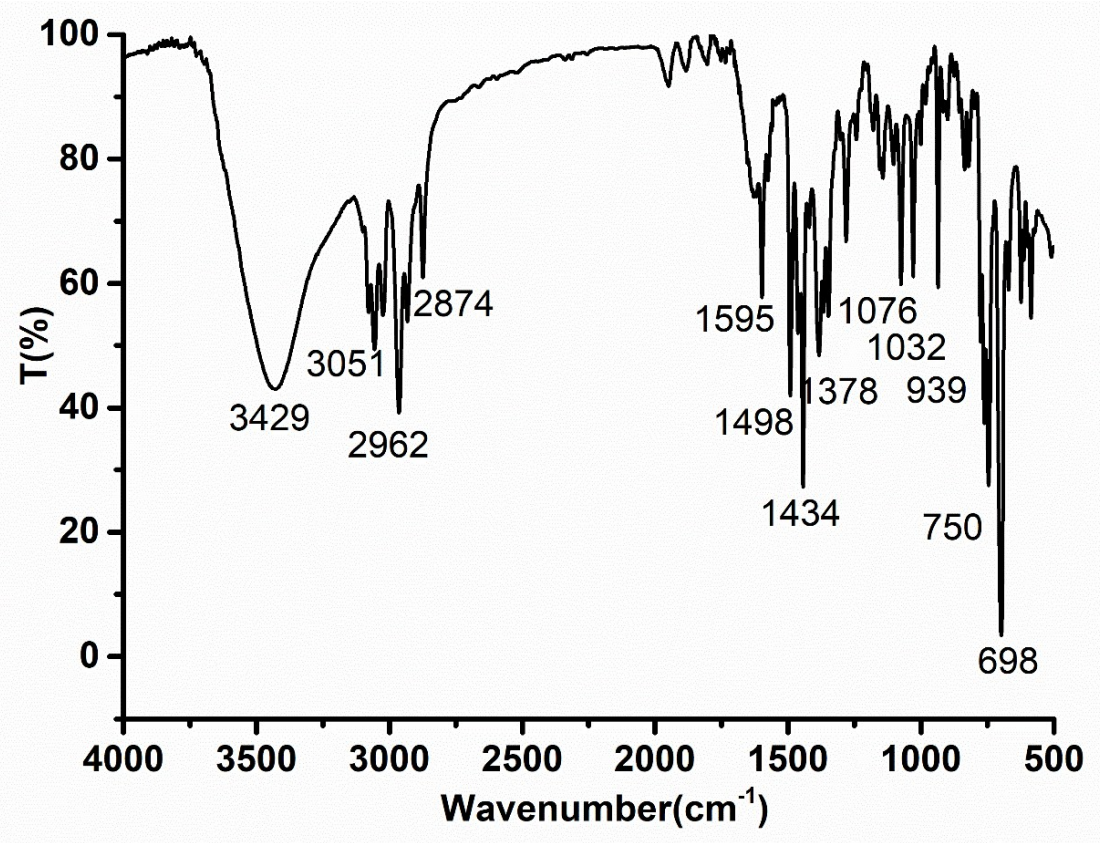


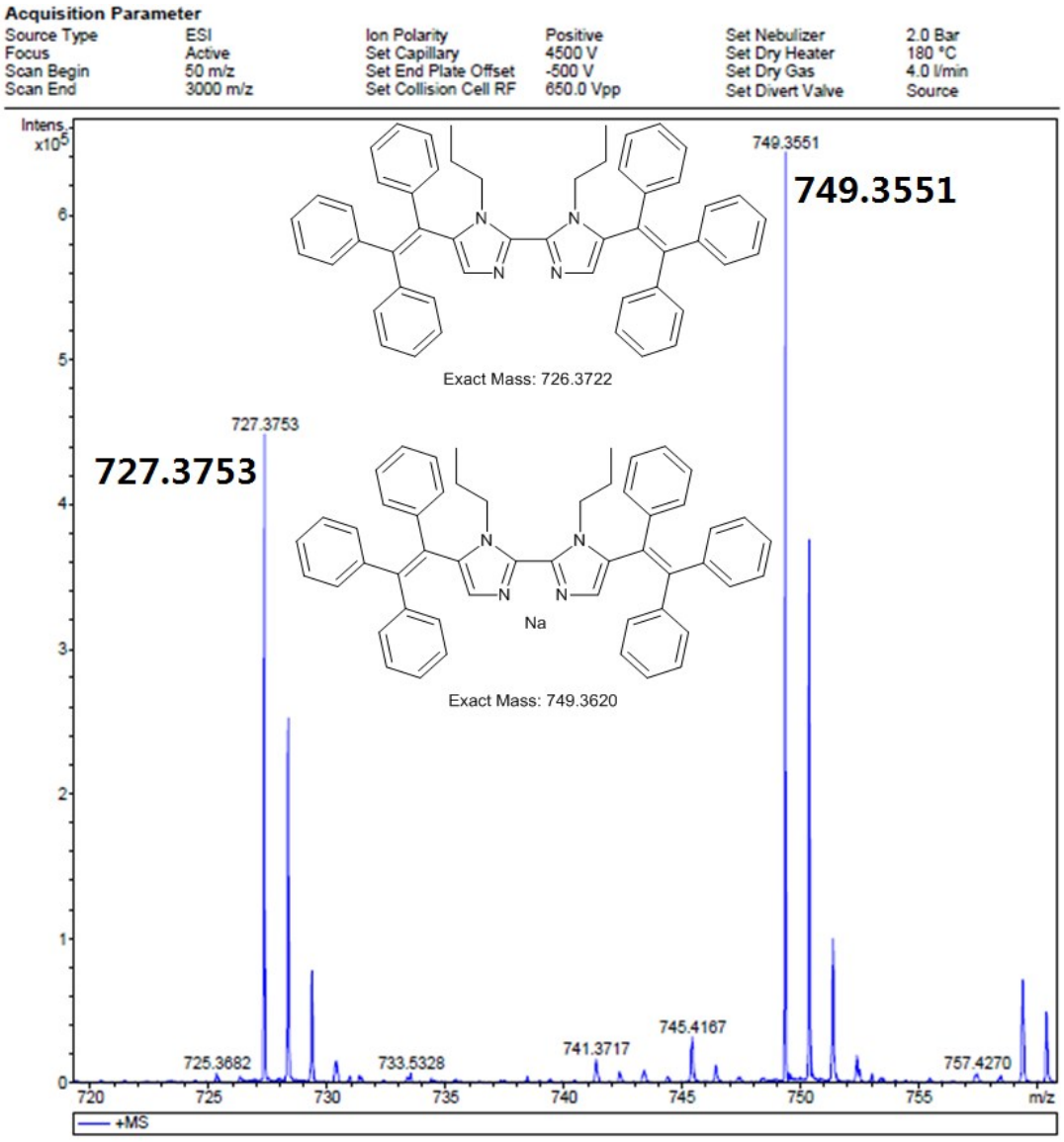
Fig. S4. ^{1}H NMR of compound **2b**.


7.11
7.06
7.04
7.03
6.61
3.76
3.75
3.73
1.57
1.28
1.26
0.60
0.59
0.57
0.07
-0.00
30.00
2.00
4.00
4.00
6.00
f1 (ppm)

a

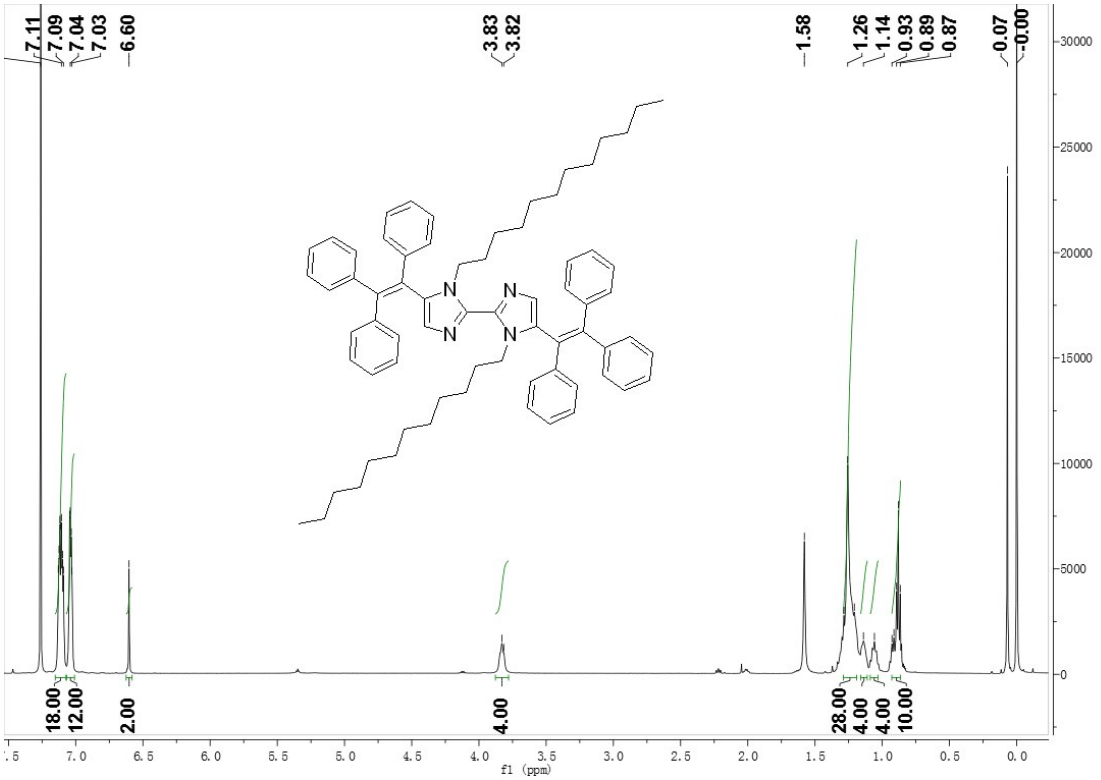

T(%)
Wavenumber(cm-1)
3429
3051
2962
2874
1595
1498
1434
1378
1076
1032
939
750
698

b

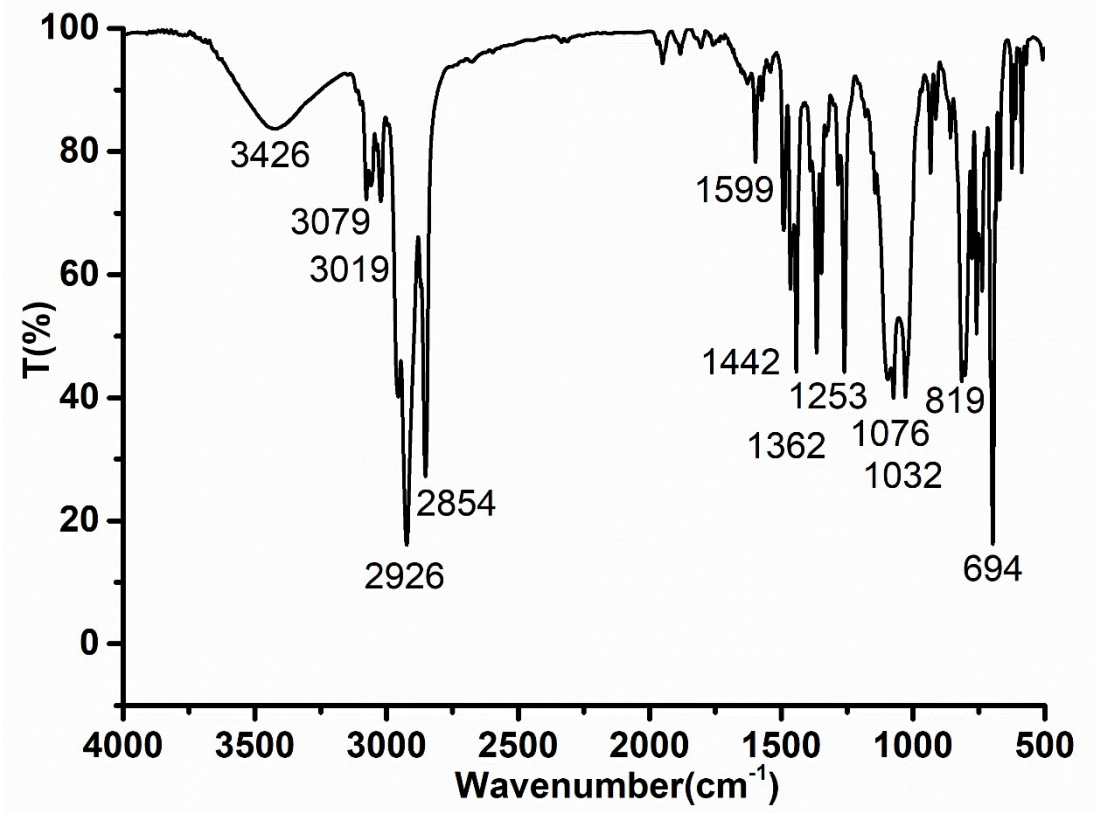


c

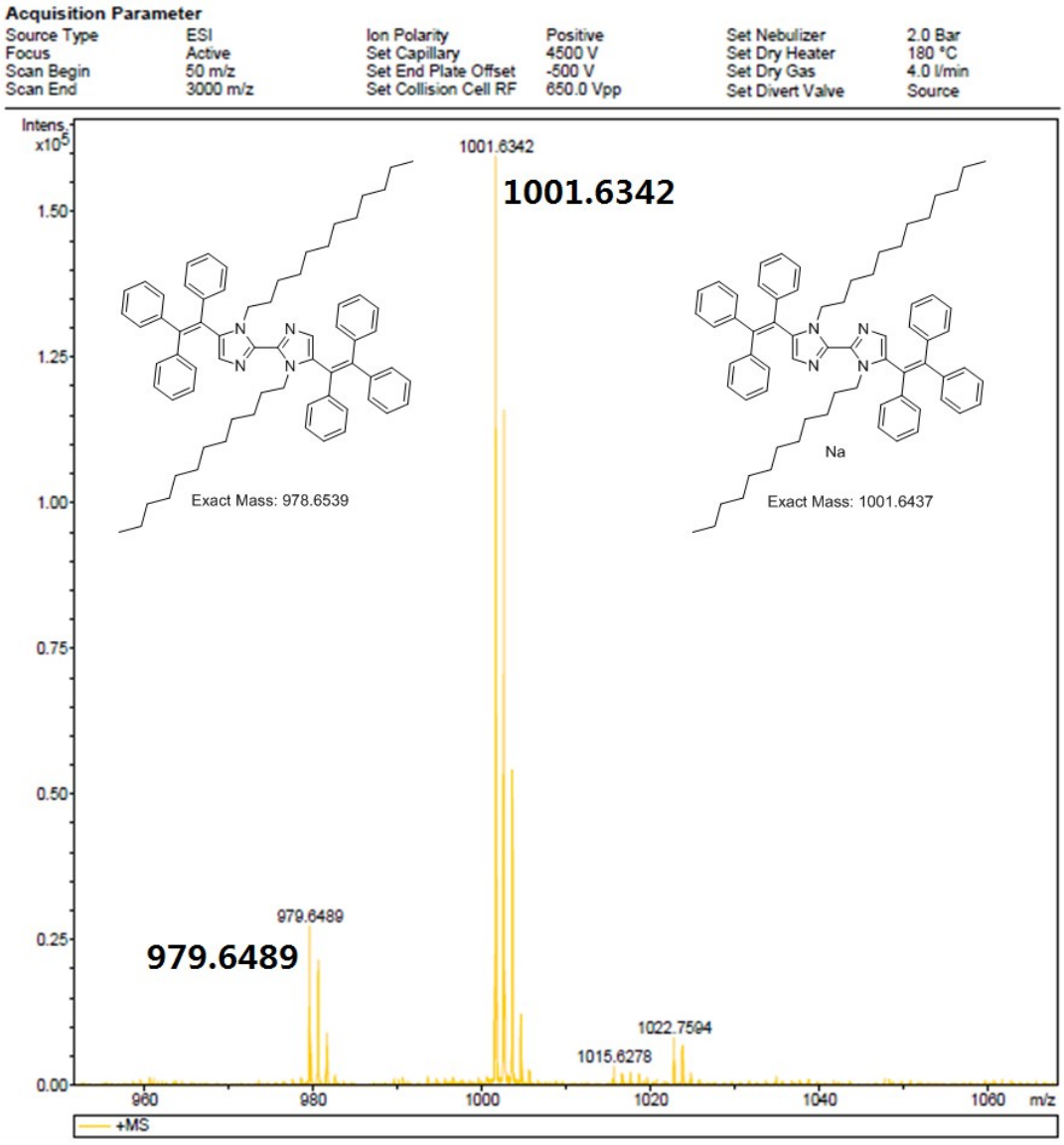
Fig. S5. ^{1}H NMR (a), FT−IR (b) and ESI−MS (c) of compound **1**.


7.11
7.09
7.04
7.03
6.60
3.83
3.82
1.58
1.26
1.14
0.93
0.89
0.87
0.07
0.00
18.00
12.00
2.00
4.00
28.00
4.00
4.00
10.00
f1 (ppm)

a

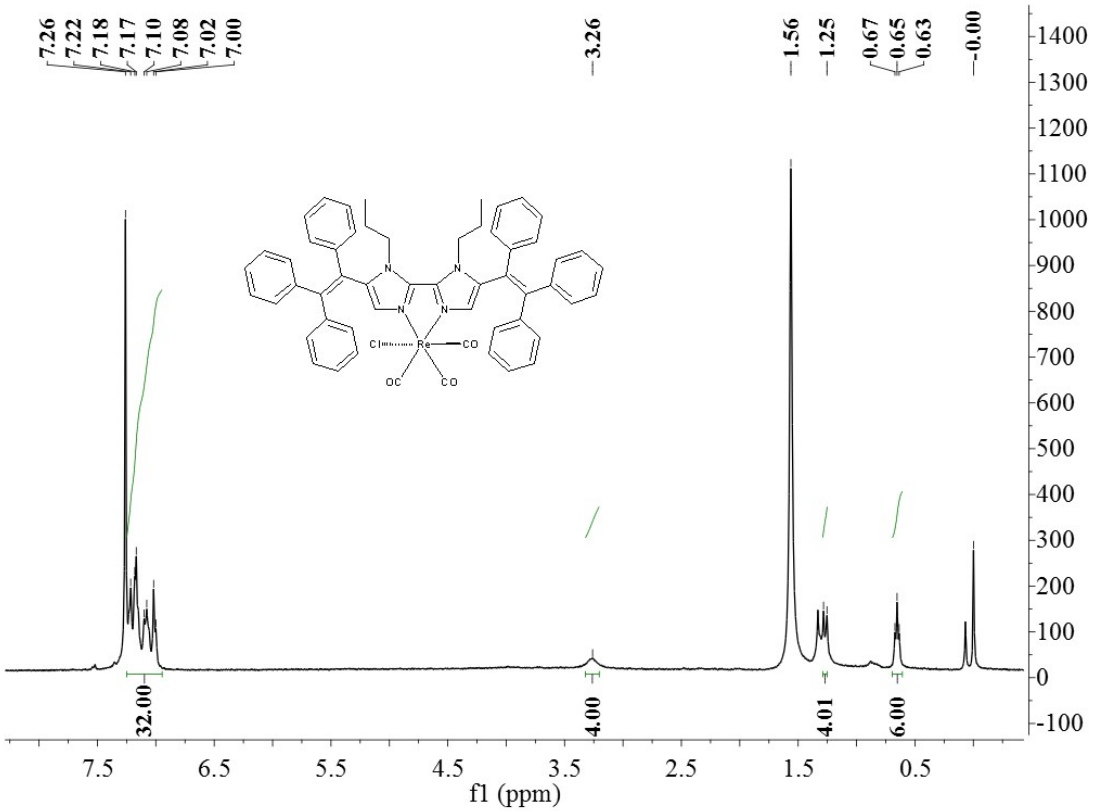

T(%)
Wavenumber(cm-1)
3426
3079
3019
2926
2854
1599
1442
1362
1253
1076
1032
819
694

b

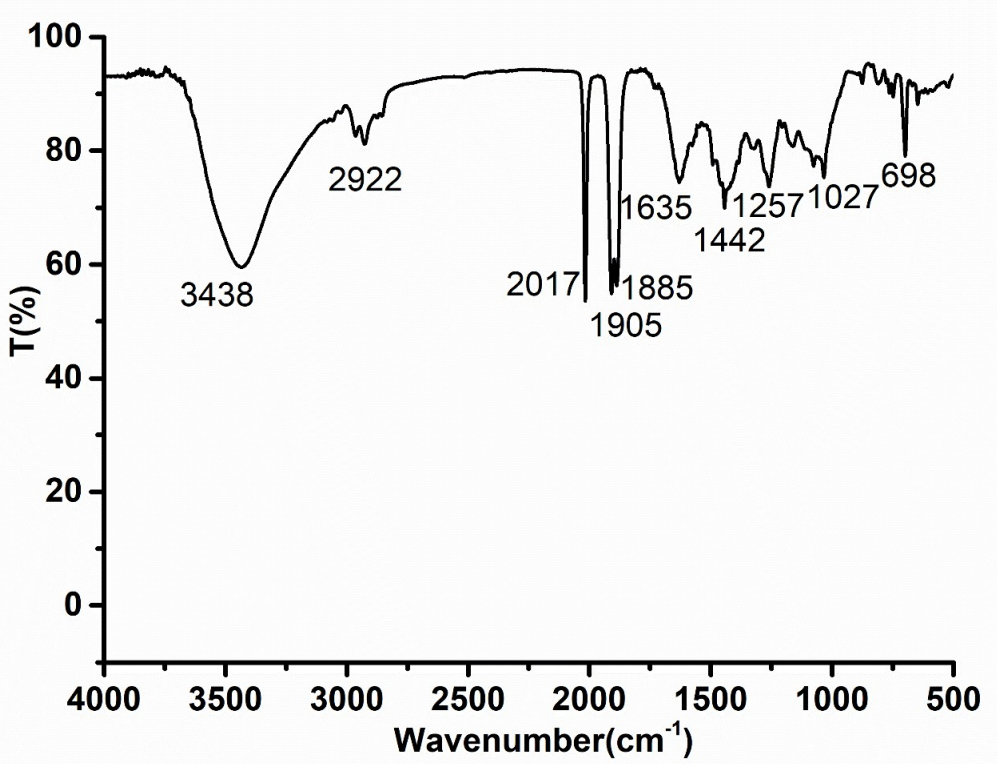


c

Fig. S6. ^{1}H NMR (a), FT−IR (b) and ESI−MS (c) of compound **2**.

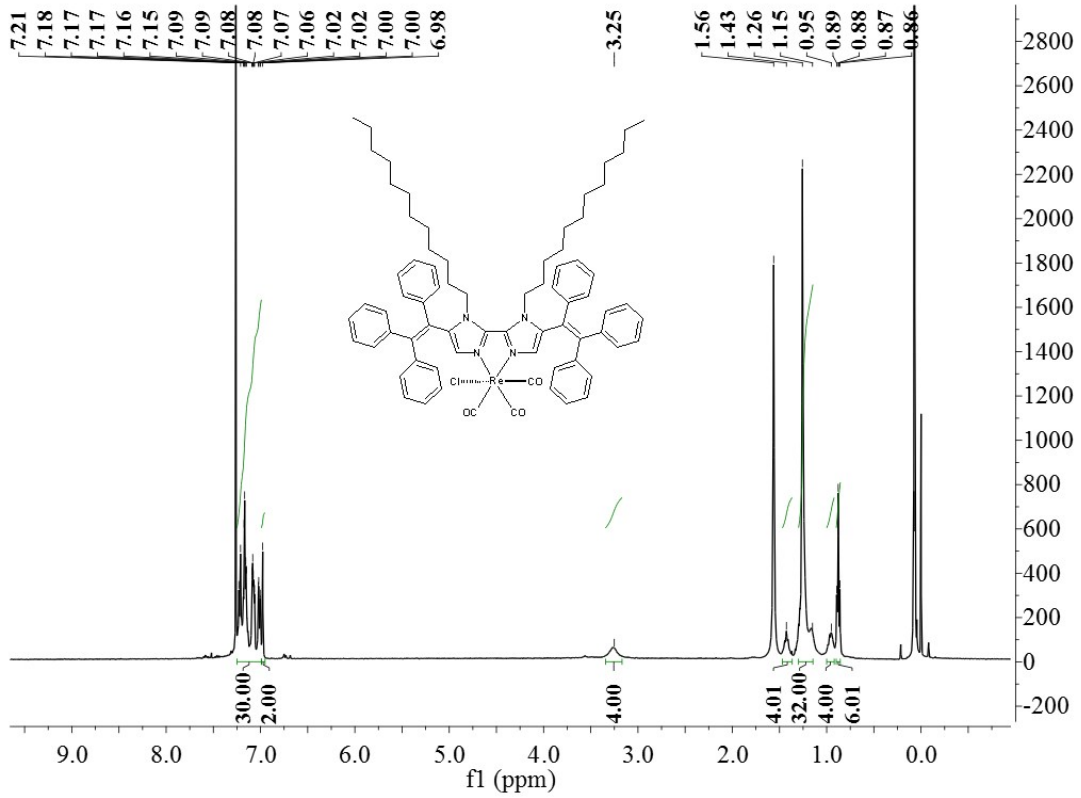


a

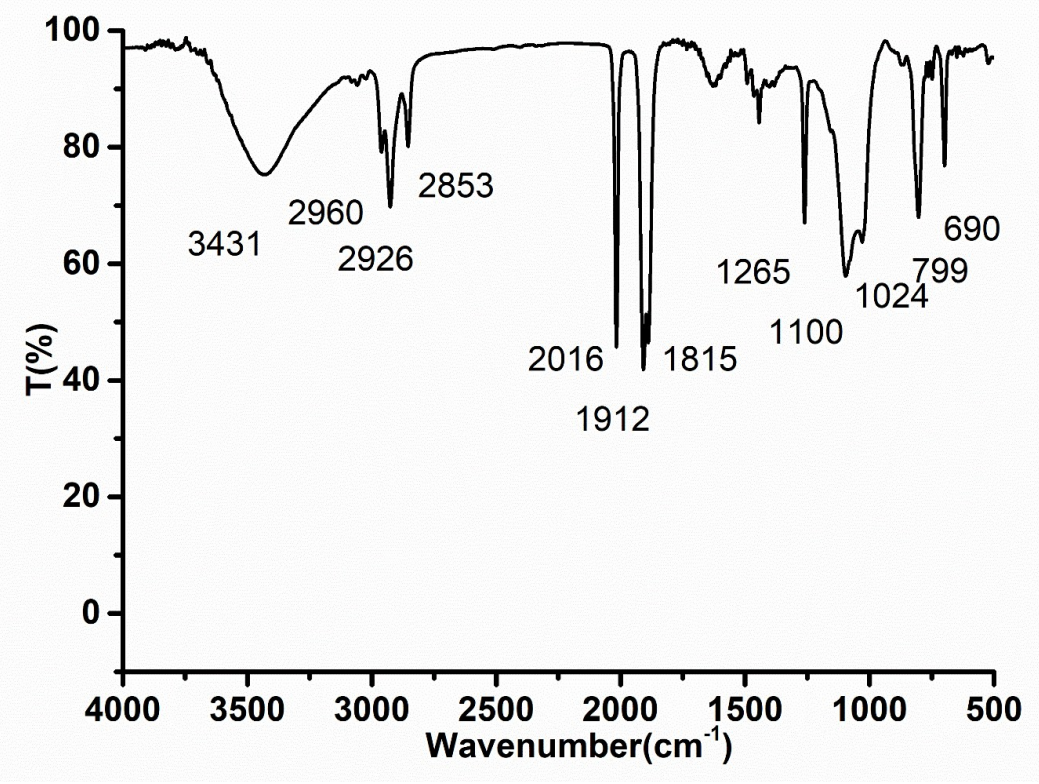


b

Fig. S7. ^{1}H NMR (a) and FT−IR (b) of compound **Re1**.



a



b

Fig. S8. ^{1}H NMR (a) and FT−IR (b) of compound **Re2**.

Table S1 Crystal data and structural refinements for compound **1** and complex **Re1·2(CHCl$_3$)**.

Compound	**1**	**Re1·2(CHCl$_3$)**
formula	$C_{52}H_{46}N_4$	$C_{57}H_{48}Cl_7N_4O_3Re$
formula wt.	726.93	1271.35
T [K]	293(2)	293(2)
wavelength / Å	0.71073	0.71073
crystal size (mm)	0.10×0.08×0.06	0.10×0.10×0.08
crystal system	Triclinic	Monoclinic
space group	$P\bar{1}$	$C2/c$
a [Å]	9.4321(18)	24.9354(12)
b [Å]	11.805(2)	10.9203(6)
c [Å]	12.282(2)	20.9330(12)
α [°]	94.069(4)	90
β [°]	90.556(4)	101.717(1)
γ [°]	101.720(3)	90
V [Å^3]	1335.3(4)	5581.3(5)
Z / D_{calcd} (g/cm^3)	1 / 0.904	4 / 1.513
F(000)	386	2544
μ [mm^{-1}]	0.053	2.559
h_{min} / h_{max}	-10 / 11	-27 / 29
k_{min} / k_{max}	-14 / 13	-12 / 12
l_{min} / l_{max}	-14 / 11	-24 / 17
data / parameter	4445 / 254	4880 / 354
final R indices	R_1 = 0.1427	R_1 = 0.0315
[$I > 2\acute{o}(I)$]	wR_2 = 0.3729	wR_2 = 0.0803
R indices	R_1 = 0.1644	R_1 = 0.0357
(all data)	wR_2 = 0.4100	wR_2 = 0.0823
S	1.00	1.10
max / min $\Delta\rho$ [e·Å^{-3}]	0.41 / -0.39	0.83 / -1.07

$R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$, $wR_2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$

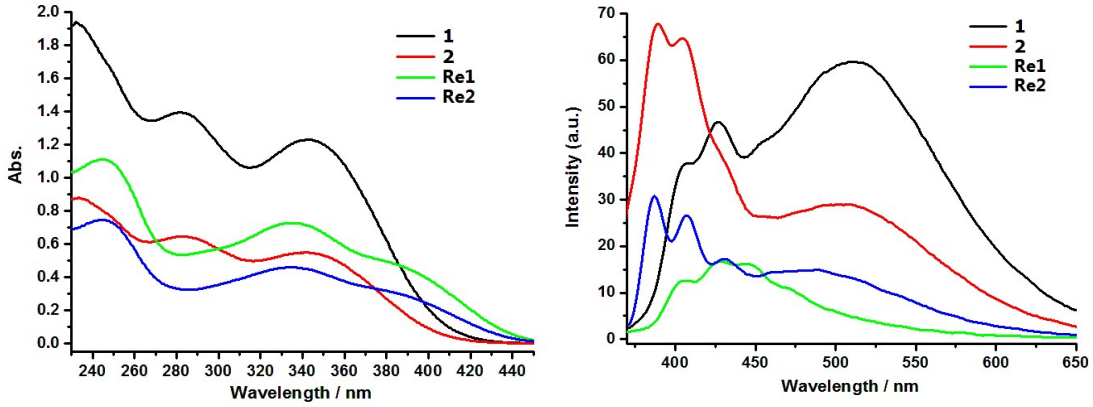
Table S2 Selected bond distances and angles (Å, °) for compound **1** and complex **Re1·2(CHCl$_3$)**.

Bond distances		Bond angles	
1			
N1–C1	1.342(5)	C1–N1–C2	105.7(3)
N1–C2	1.341(5)	C1–N2–C3	108.4(3)
N2–C1	1.373(4)	C1–N2–C24	126.8(3)
N2–C3	1.397(4)	C3–N2–C24	124.5(3)
N2–C24	1.462(5)	N1–C1–N2	110.3(3)
C1–C1^a	1.444(5)	N1–C1–C1^a	124.7(3)
		N2–C1–C1^a	125.0(3)
		N1–C2–C3	112.9(3)
		N2–C3–C2	102.7(3)
		N2–C3–C4	126.9(3)
Re1·2(CHCl$_3$)			
Re1–Cl1	2.491(4)	Cl1–Re1–N1	84.86(10)
Re1–N1	2.153(3)	Cl1–Re1–C24	96.16(19)
Re1–C24	1.918(5)	Cl1–Re1–N1b	81.40(10)
Re1–C25	1.861(14)	Cl1–Re1–C24^b	96.2(2)
O1–C24	1.151(6)	N1–Re1–C24	99.54(16)
O2–C25	1.139(17)	N1–Re1–C25	93.0(3)
N1–C1	1.343(5)	N1–Re1–N1^b	73.08(11)
N1–C2	1.367(5)	N1–Re1–C25^b	92.0(3)
N2–C26	1.473(6)	C24–Re1–C25	86.4(4)
N2–C1	1.364(4)	N1^b–Re1–C24	172.35(16)
N2–C3	1.389(4)	C24–Re1–C24^b	87.91(19)
C1–C1^b	1.456(4)	C25–Re1–C25^b	173.9(5)

Symmetry Code: ^{a} -*x*, 1-*y*, 2-*z*; ^{b} -*x*, *y*, 1/2-*z*.

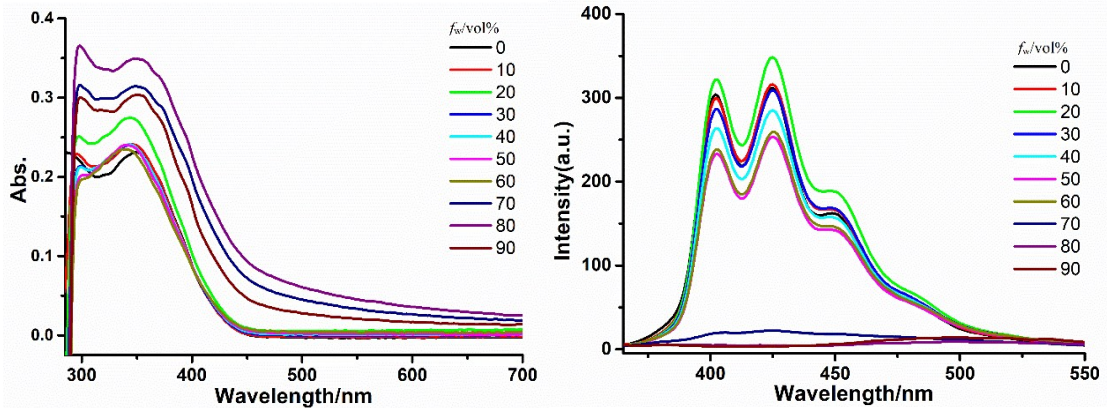
Table S3 Hydrogen bonding interactions (Å, °) for compound **1** and complex **Re1·2(CHCl$_3$)**.

D–H···A	D–H	H···A	D···A	∠DHA	Symmetry Code
1					
C24–H24A···N1	0.97	2.20	2.911(6)	129.0	*-x*,1-*y*,2-*z*
Re1·2(CHCl$_3$)					
C7–H7···O2	0.93	2.50	3.067(11)	120.0	*x*,1-*y*,-1/2+*z*
C29–H29···O2	0.93	2.54	3.369(12)	148.0	*x*,1-*y*,-1/2+*z*



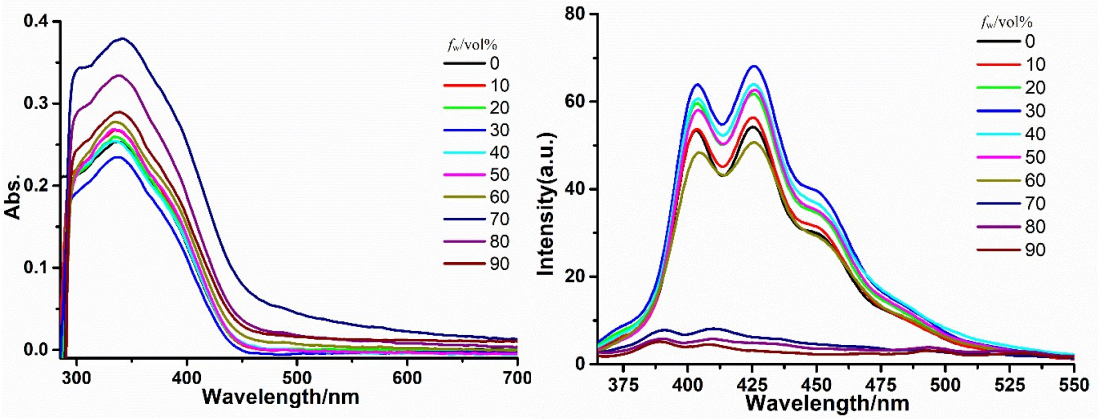
a **b**

Fig. S9. Absorption (a) and emission (b) spectra of two biimidazole ligands and their rhenium complexes in dichloromethane solutions.



a **b**

Fig. S10. UV–Vis absorption spectra (a) and fluorescence emission spectra (b) for complex **Re1** in THF/water mixtures with the same concentration of 1.0×10^{-5} mol·L^{-1} and different water volume fractions (f_w).



a **b**

Fig. S11. UV–Vis absorption spectra (a) and fluorescence emission spectra (b) for complex **Re2** in THF/water mixtures with the same concentration of 1.0×10^{-5} mol·L^{-1} and different water volume fractions (f_w).

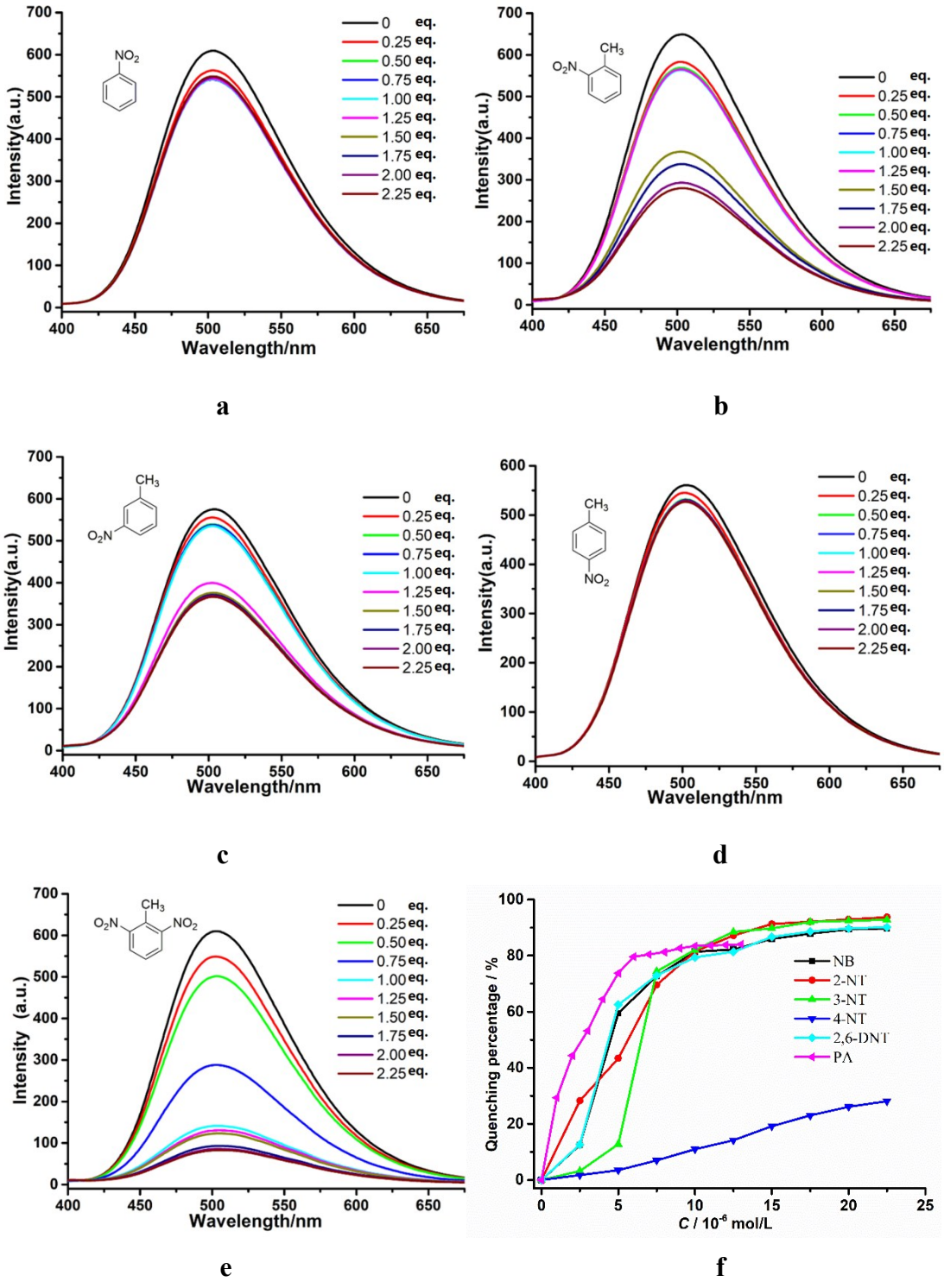
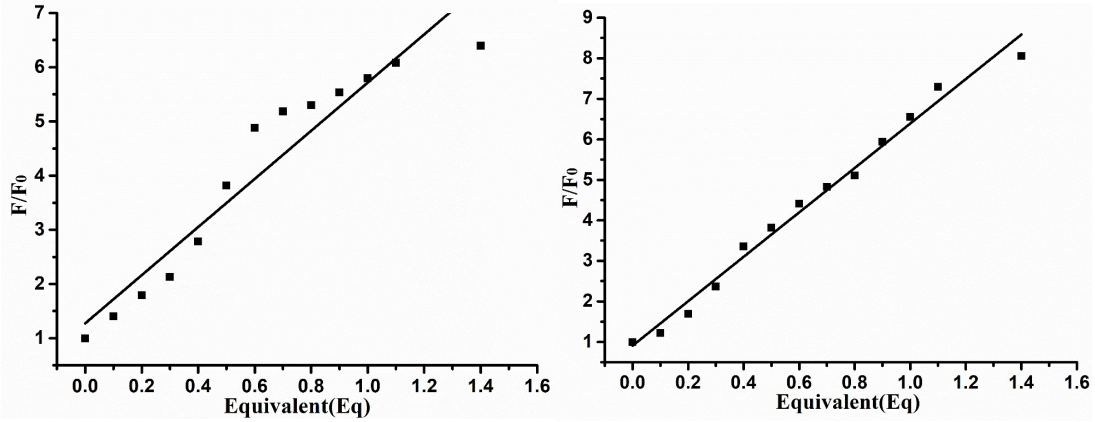


Fig. S12. Fluorescence titration spectra of compound **2** with NB (a), 2-NT (b), 3-NT (c), 4-NT (d) and 2,6-DNT (e) in THF/water mixtures where f_w = 90%; (f) Quenching percentage plot of compound **2** with different guest molecules.



a **b**

Fig. S13. Fluorescence titration fitting plot for AIEgens **1** (a) and **2** (b) with the addition of different equivalents of PA in solution in order to calculate the limit of detection.