Supplementary Information

Aggregation-induced emission of bis(imino)acenaphthene zinc complex with tetraphenylethene units

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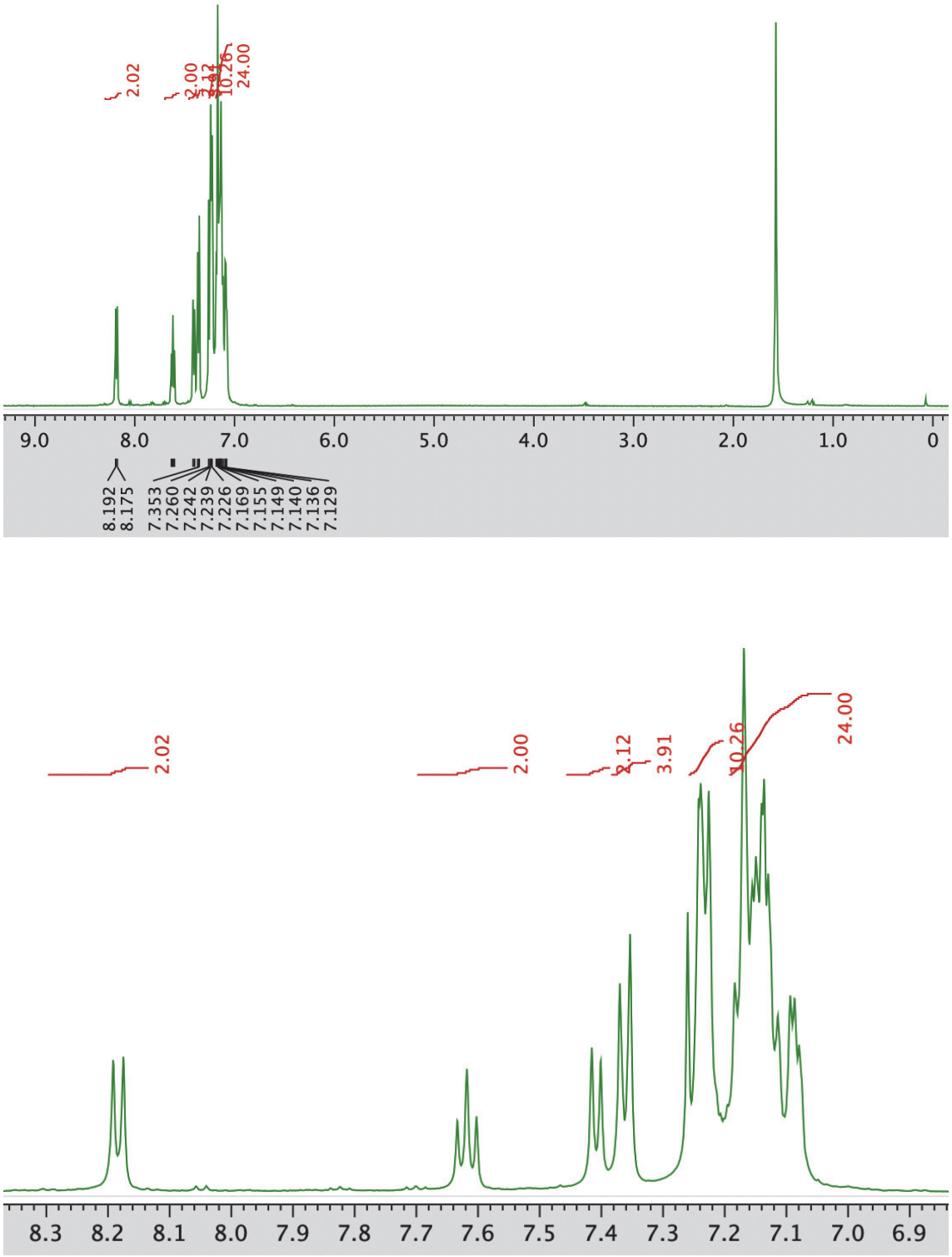


Fig. S1 ^{1}H NMR spectrum of zinc complex **Zn-2** (500 MHz, in $CDCl_3$).

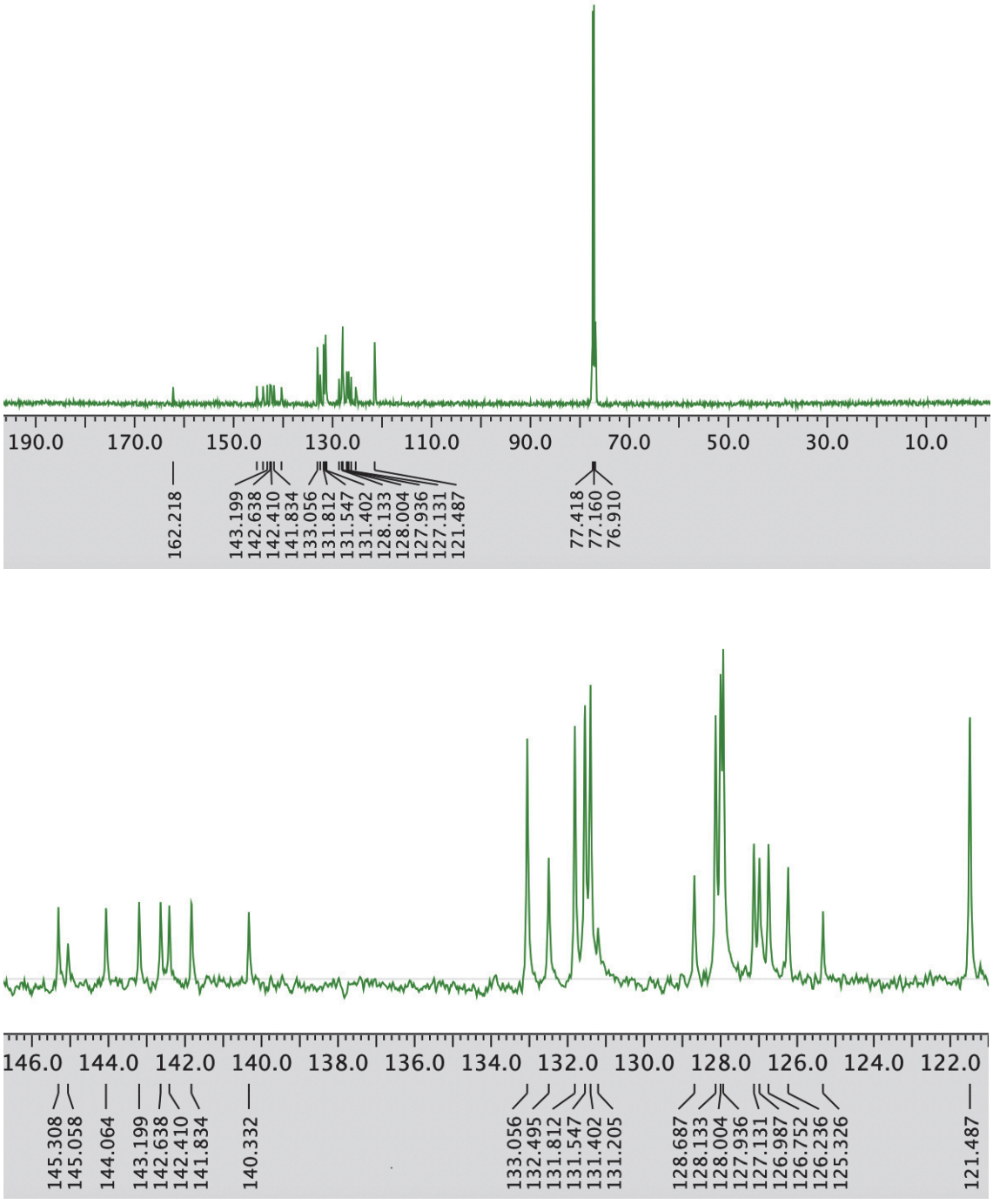


Fig. S2 ^{13}C NMR spectrum of zinc complex **Zn-2** (125 MHz, in $CDCl_3$).

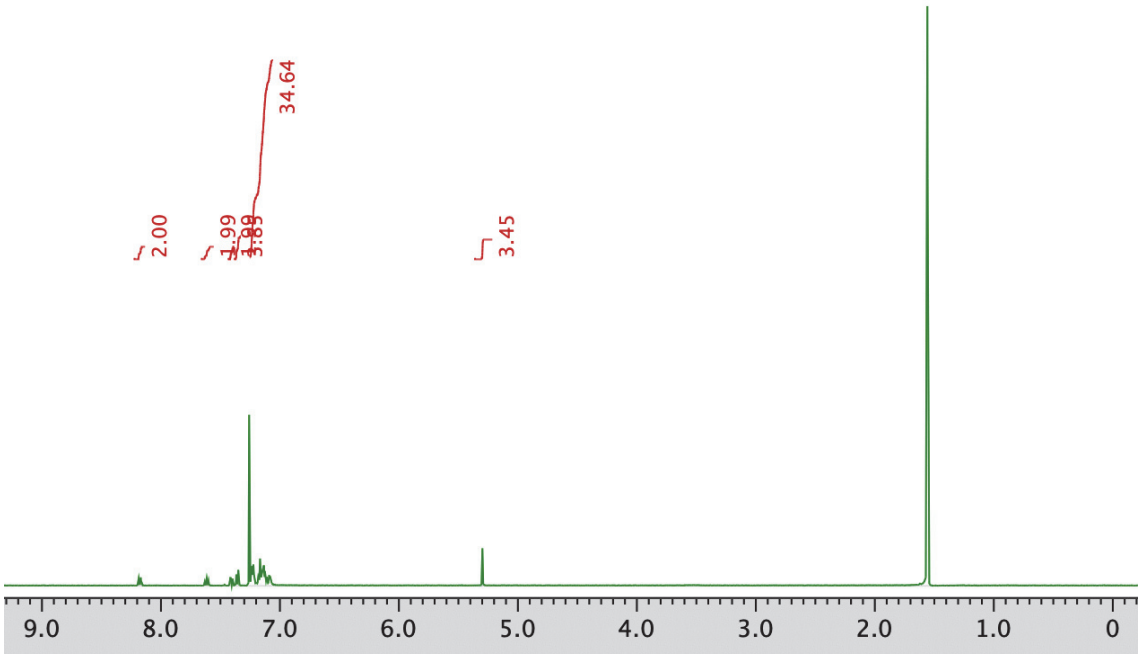


Fig. S3 ^{1}H NMR spectrum of **Zn-2-DCM** (500 MHz, in $CDCl_3$).

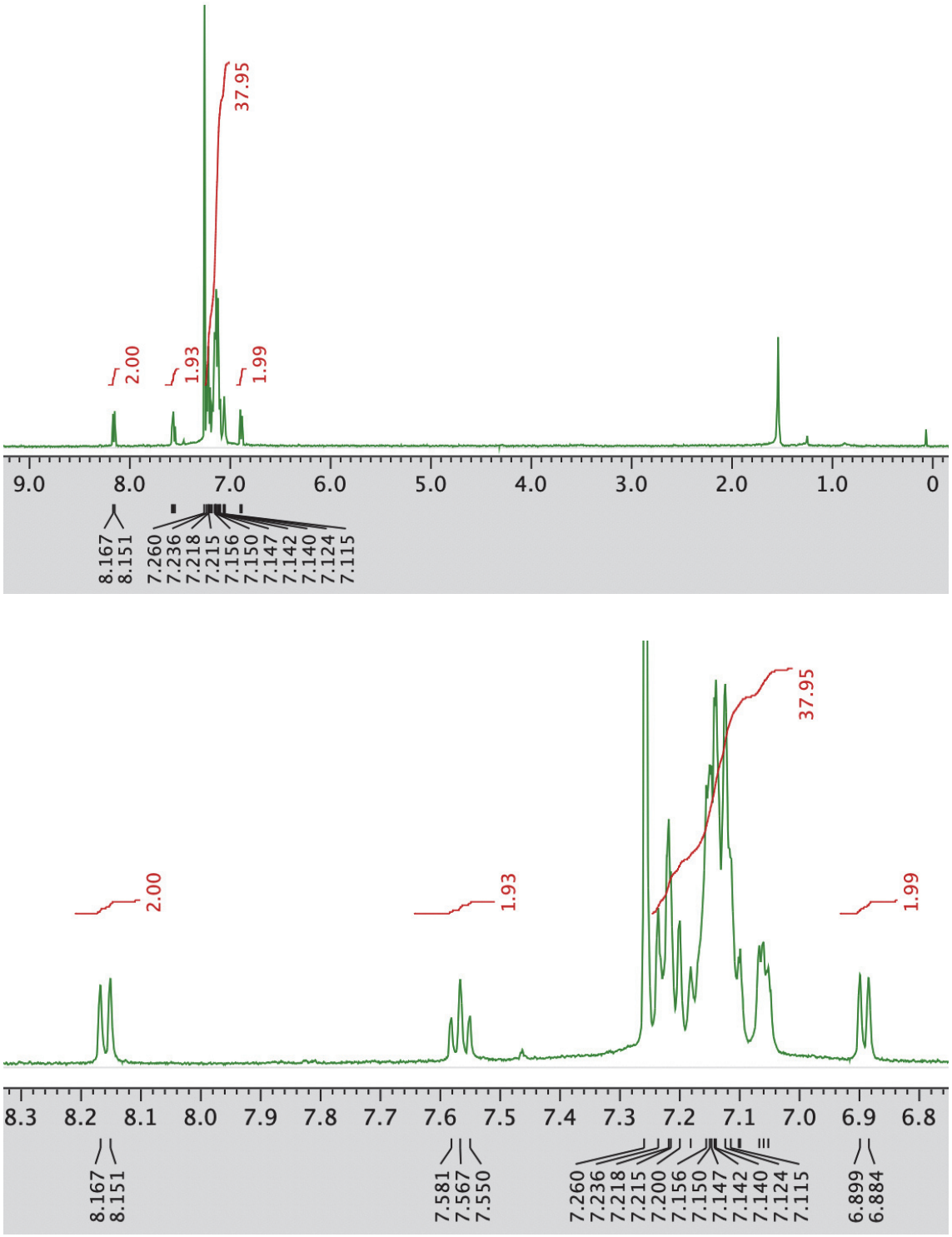


Fig. S4 ^{1}H NMR spectrum of palladium complex **Pd-2** (500 MHz, in $CDCl_3$).

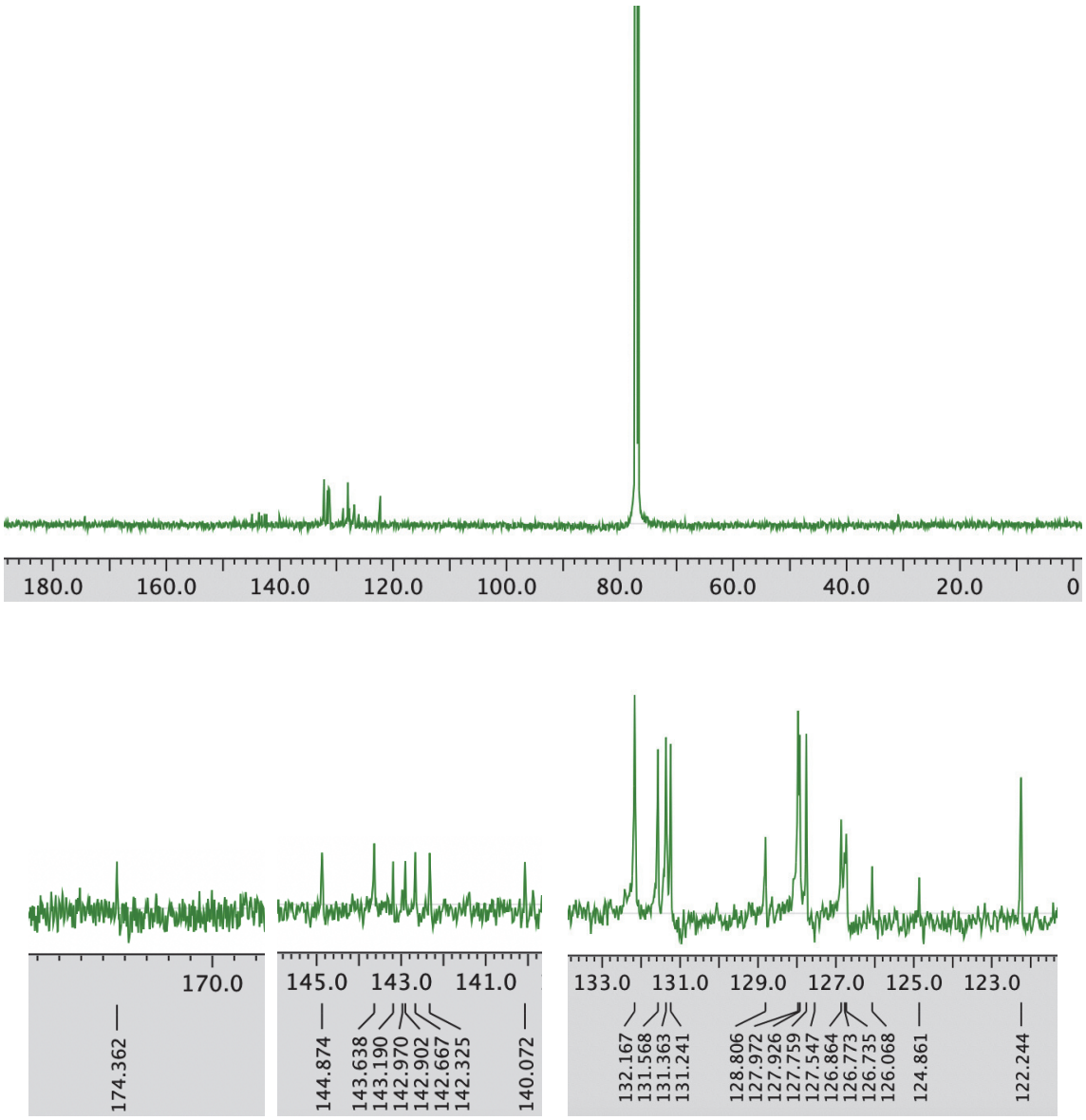


Fig. S5 ^{13}C NMR spectrum of palladium complex **Pd-2** (500 MHz, in $CDCl_3$).

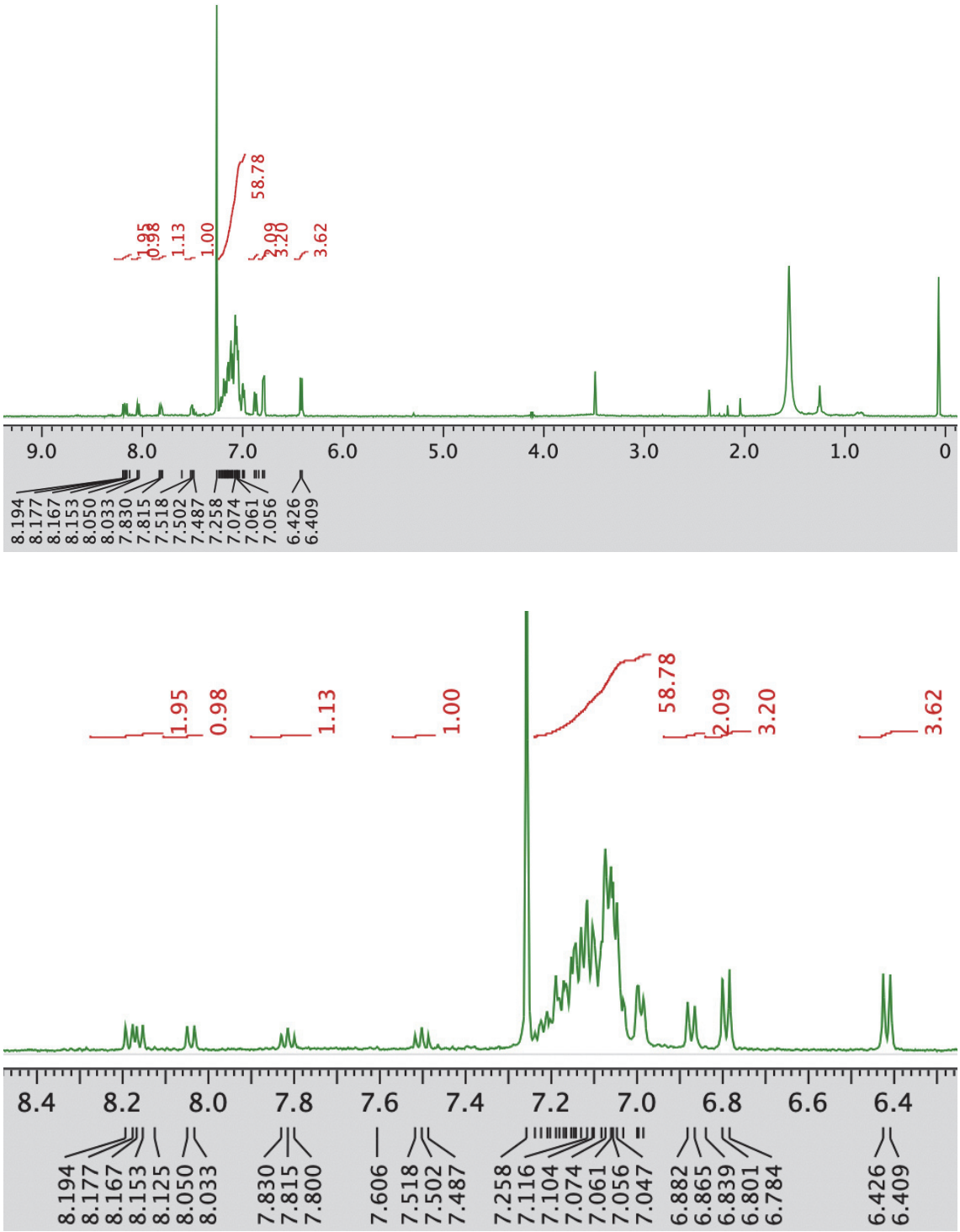


Fig. S6 ^{1}H NMR spectrum of the crude product after direct imine condensation between aniline **1** and acenaphthenequinone (500 MHz, in $CDCl_3$).

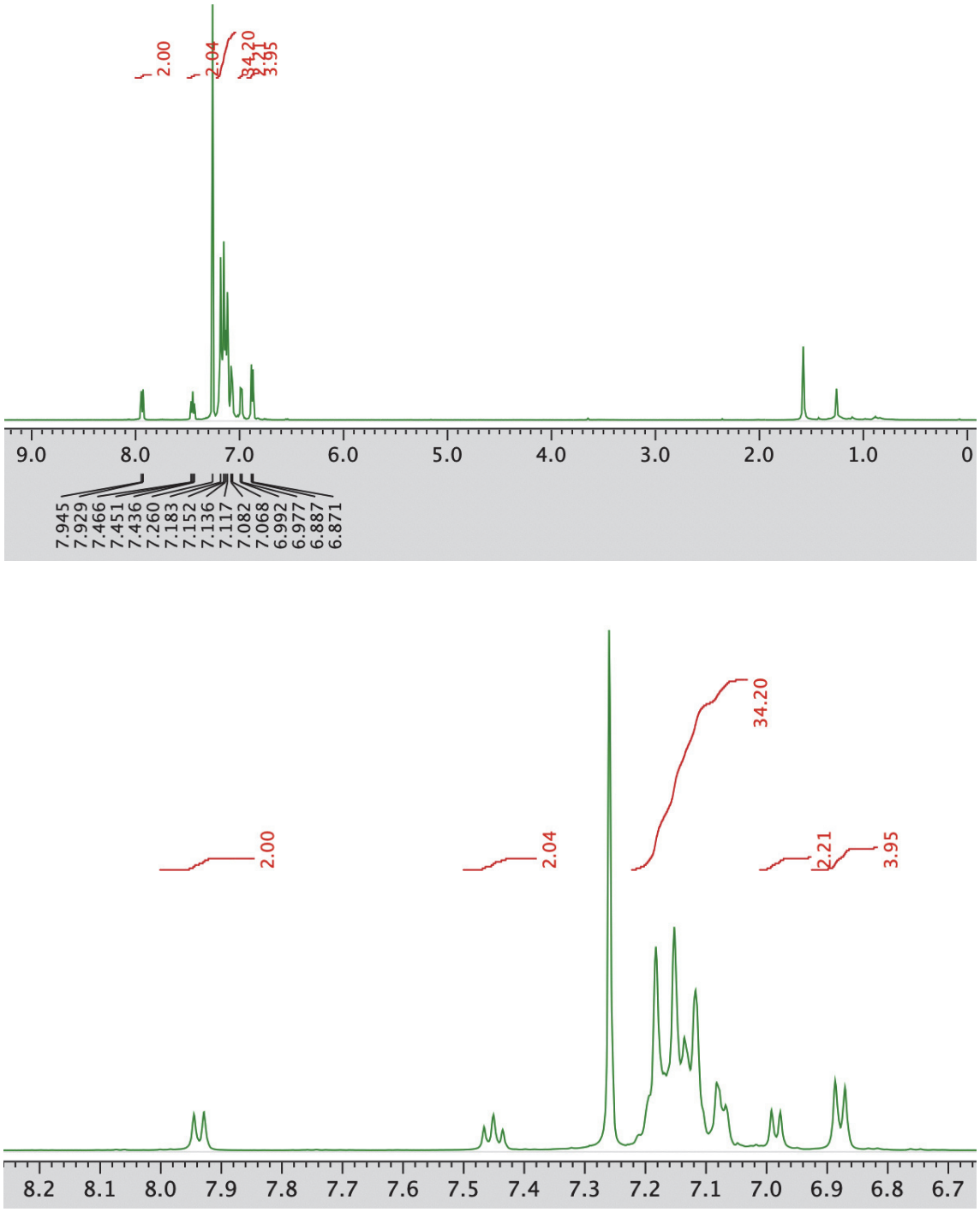


Fig. S7 ^{1}H NMR spectrum of diimine ligand **3** (500 MHz, in $CDCl_3$).

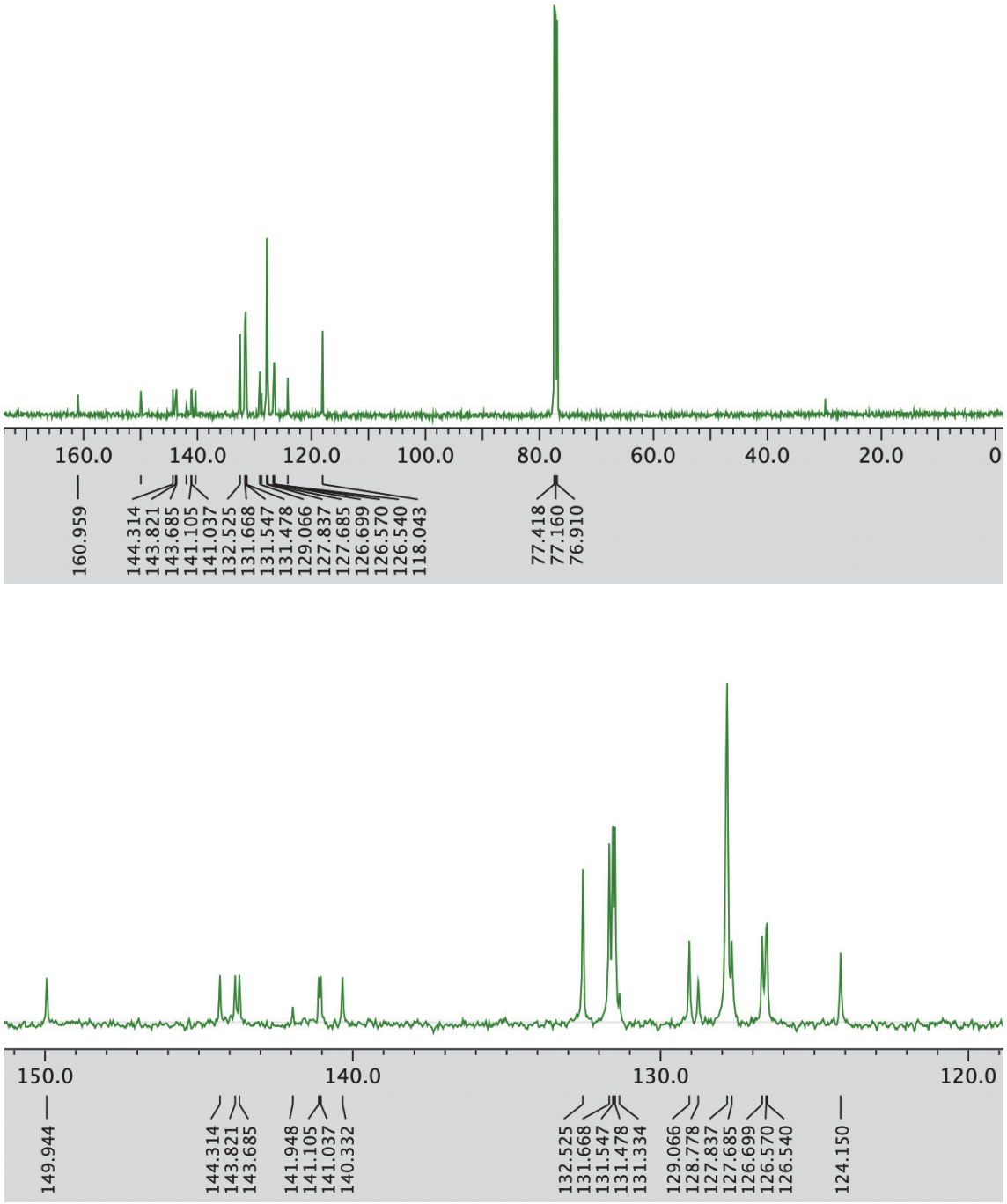
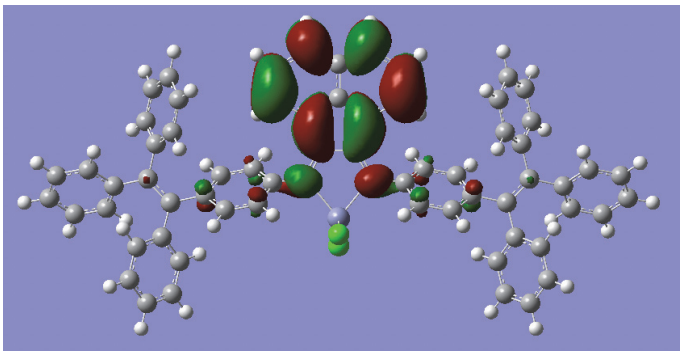


Fig. S8 ^{13}C NMR spectrum of diimine ligand **3** (125 MHz, in $CDCl_3$).

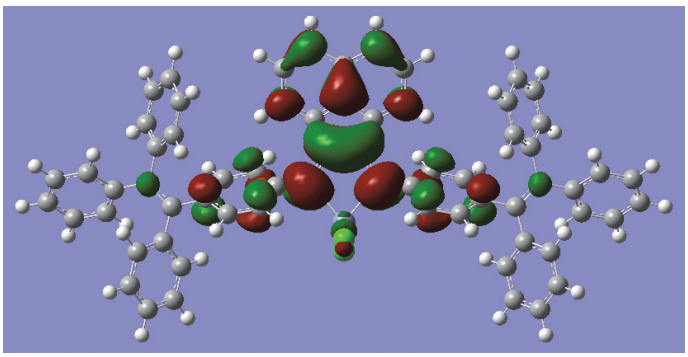
Table S1 Crystal refinement data for complexes **Zn-2-DCM** and **Pd-2-DCM**

Compound	**Zn-2-DCM**	**Pd-2-DCM**
Wavelength (Å)	0.71069 Å	0.71069 Å
Temperature (K)	123	123
Empirical formula	$C_{65}H_{46}Cl_4N_2Zn$	$C_{65}H_{46}Cl_4N_2Pd$
Formula weight	1062.21	1103.24
Crystal system	Triclinic	Triclinic
Space group	P^{-1}	P^{-1}
a (Å)	12.3907(3)	12.3224(2)
b (Å)	15.0562(3)	14.5950(3)
c (Å)	17.4004(5)	19.1625(4)
α (deg)	105.345(2)	102.491(2)
β (deg)	105.894(2)	92.773(1)
γ (deg)	97.538(2)	109.549(2)
Volume (Å^3)	2937.28(13)	3143.33(11)
Z	2	2
D_{calc} (g/cm^3)	1.201	1.166
μ (mm^{-1})	0.639	0.502
F(000)	1096.0	1128.0
Crystal size (mm)	0.23 x 0.15 x 0.15	0.30 x 0.13 x 0.12
θ_{max} (deg)	31.527	29.822
Index ranges	-17 ≤ h ≤ 17	-16 ≤ h ≤ 16
	-19 ≤ k ≤ 21	-20 ≤ k ≤ 20
	-24 ≤ l ≤ 24	-26 ≤ l ≤ 26
No. of reflections observed	16552	15714
No. of parameters refined	649	748
T_{min}, T_{max}	0.656, 1.000	0.674, 1.000
R_1	0.0671	0.0494
wR_2	0.1765	0.1444
GoF on F^2	1.027	1.056

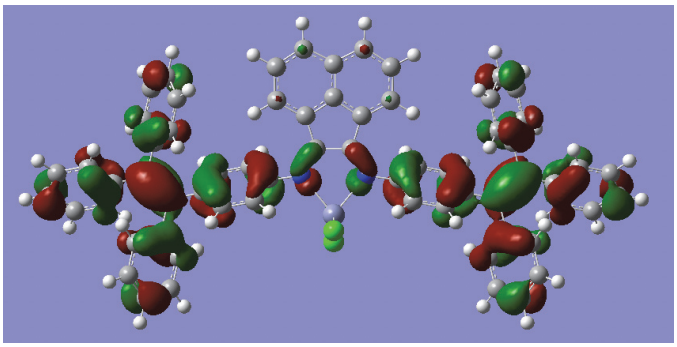
LUMO+1(255)



LUMO(254)



HOMO (253)



HOMO-1 (252)

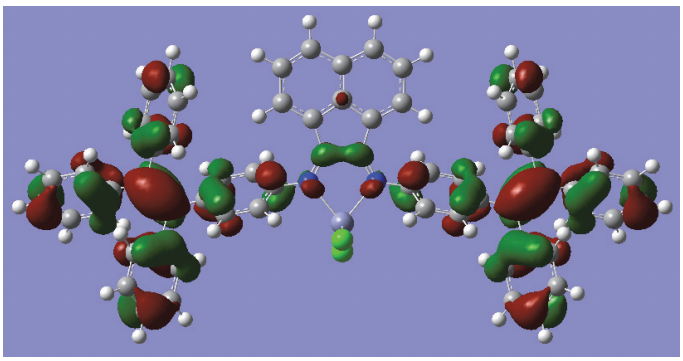
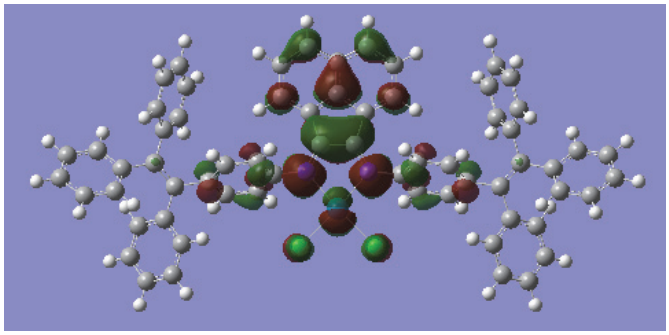
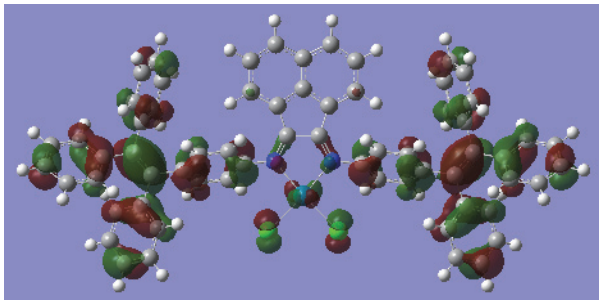


Fig. S9 Calculated frontier orbitals of **Zn-2** derived from DFT calculations at the cc-pVTZ level.

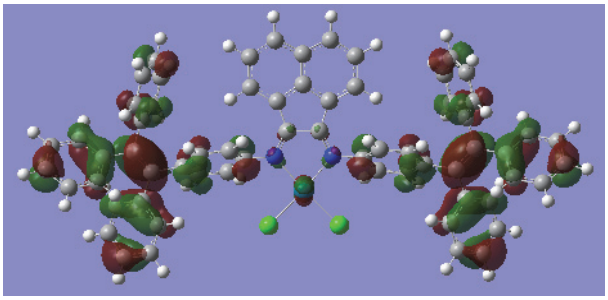
LUMO (248)



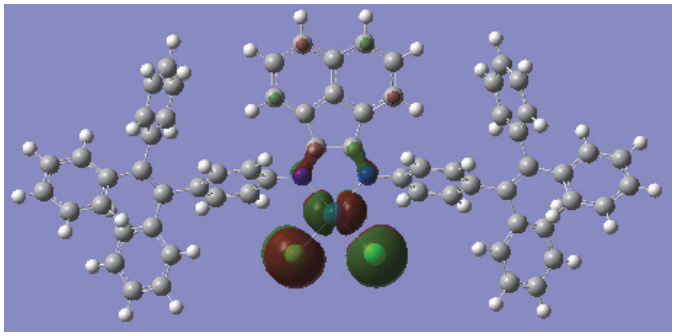
HOMO (247)



HOMO-1 (246)



HOMO-2 (245)



HOMO-4 (243)

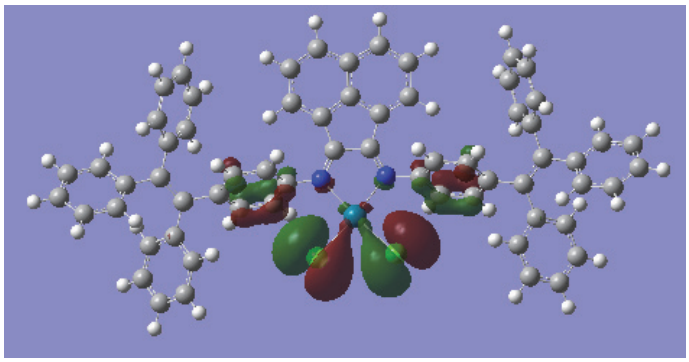
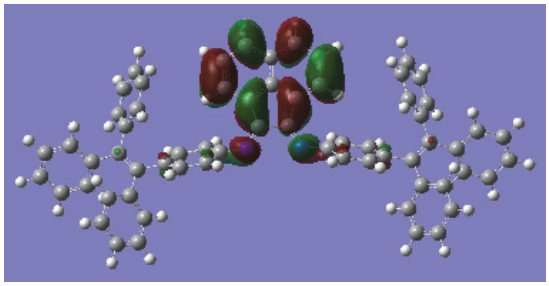
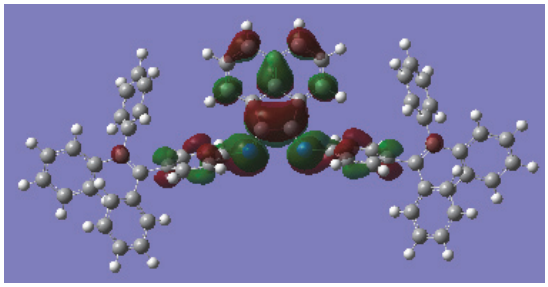


Fig. S10 Calculated frontier orbitals of **Pd-2** derived from DFT calculations at the cc-pVTZ-PP (Pd) / cc-pVTZ (other atoms) level.

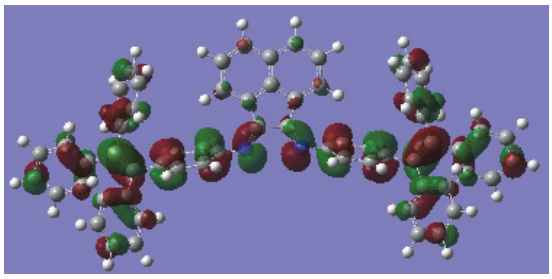
LUMO+1(223)



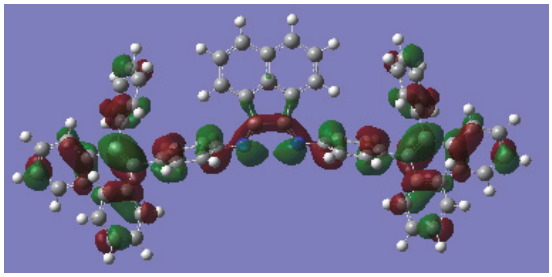
LUMO(222)



HOMO (221)



HOMO-1 (220)



HOMO-2 (219)

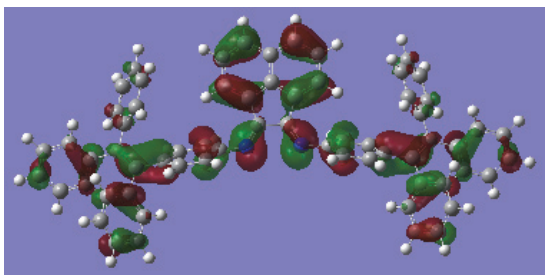


Fig. S11 Calculated frontier orbitals of **3** derived from DFT calculations at the cc-pVTZ level.

Table S2 Calculated electronic transition to the singlet excited states in **Zn-2** by TD-DFT method.

1.5914 eV	779.08 nm	f=0.3586	<S**2>=0.000
253 -> 254		0.70650	
1.7217 eV	720.12 nm	f=0.0090	<S**2>=0.000
252 -> 254		0.70499	
2.1052 eV	588.94 nm	f=0.0106	<S**2>=0.000
253 -> 255		0.70393	
2.1974 eV	564.24 nm	f=0.0348	<S**2>=0.000
252 -> 255		0.70604	

Table S3 Calculated electronic transition to the singlet excited states in **Pd-2** by TD-DFT method.

1.5004 eV	826.34 nm	f=0.1288	<S**2>=0.000
245 -> 248		0.24682	
247 -> 248		0.65900	
1.5817 eV	783.88 nm	f=0.0019	<S**2>=0.000
246 -> 248		0.70147	
1.5889 eV	780.34 nm	f=0.0623	<S**2>=0.000
245 -> 248		0.65657	
247 -> 248		-0.24945	
1.8268 eV	678.70 nm	f=0.0010	<S**2>=0.000
243 -> 248		0.70396	

Table S4 Calculated electronic transition to the singlet excited states in **3** by TD-DFT method.

2.0994 eV	590.57 nm	f=0.3159	<S**2>=0.000
221 -> 222		0.70257	
2.2441 eV	552.50 nm	f=0.0106	<S**2>=0.000
220 -> 222		0.70178	
2.4012 eV	516.34 nm	f=0.0127	<S**2>=0.000
221 -> 223		0.70455	
2.5090 eV	494.16 nm	f=0.0281	<S**2>=0.000
220 -> 223		0.70317	
2.9013 eV	427.34 nm	f=0.0747	<S**2>=0.000
217 -> 222		0.15618	
219 -> 222		0.67011	

Table S5 Calculated electronic transition to the triplet excited states in **Zn-2** by TD-DFT method.

1.3249 eV	935.82 nm	f=0.0000	<S**2>=2.000
248 -> 254		-0.14758	
250 -> 254		0.12078	
253 -> 254		0.66548	
1.5123 eV	819.83 nm	f=0.0000	<S**2>=2.000
252 -> 254		0.67726	
253 -> 255		0.11933	
1.9405 eV	638.91 nm	f=0.0000	<S**2>=2.000
245 -> 255		-0.10086	
248 -> 255		-0.17086	
250 -> 255		0.13519	
252 -> 254		-0.16005	
253 -> 255		0.59964	

Table S6 Calculated electronic transition to the triplet excited states in **Pd-2** by TD-DFT method.

1.2761 eV	971.55 nm	<S**2>=2.000
240 -> 248		-0.12167
245 -> 248		0.47529
247 -> 248		0.48849
1.4508 eV	854.62 nm	<S**2>=2.000
241 -> 248		-0.10813
242 -> 248		0.11947
246 -> 248		0.67444
1.4648 eV	846.41 nm	<S**2>=2.000
245 -> 248		0.50888
247 -> 248		-0.47867

Table S7 Energy differences in singlet and triplet states located by DFT/U-DFT methods.

Complex	Energy of singlet state (Hartree)	Energy of triplet state (Hartree)	$\Delta(T_1\text{-}S_0)$ (eV)
Zn-2	-5276.12136791	-5276.07822399	1.1739
Pd-2	-3624.10462688	-3624.06007376	1.2123

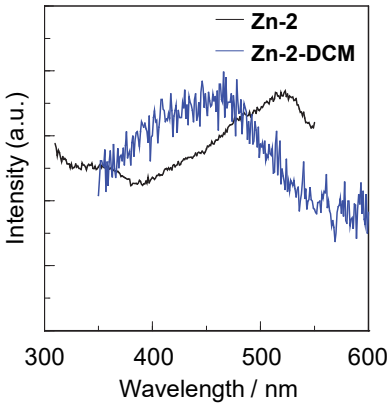


Fig. S12 Solid-state photoexcitation spectra of **Zn-2** and **Zn-2-DCM** in the solid state.

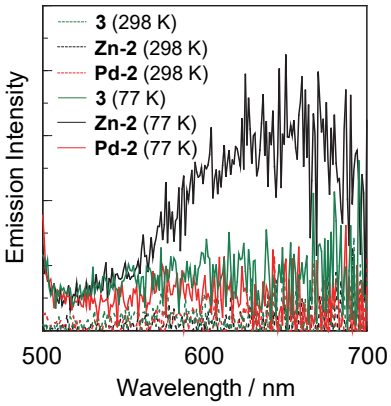


Fig. 13 Emission spectra (λ^{ex} = 490 nm) of **3**, **Zn-2** and **Pd-2** (1.0×10^{-4} M) in 2-MeTHF at 298 K and the glassy matrix of 2-MeTHF at 77K.