Supporting information for

Symmetry Breaking Charge Transfer of Visible Light Absorbing System

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Synthesis and Characterization:

Synthesis of homoleptic complexes *zDIP1–zDIP4*. 2,4-dimethylpyrrole (98%) and 3-ethyl-2,4-dimethylpyrrole were purchased from TCI America; 2-methylpyrrole was synthesized by published procedure; synthesis of *zDIP1* followed the literature procedures.[42] The obtained *zDIP1* was further purified by vacuum sublimation. Syntheses of *zDIP2–zDIP4* were modified from the literature procedures for *zDIP1*. The synthetic procedure for preparing *zDIP2* is given below; the same procedure was used to prepare *zDIP3* and *zDIP4*.

Bis(1,9-dimethyl-5-mesityldipyrrinato) zinc (zDIP2). A solution of mesitaldehyde (4.6 g, 30.9 mmol) and 2-methylpyrrole (5 g, 61.7 mmol) in 200 ml dichloromethane was prepared and 3 drops of trifluoroacetic acid (TFA) were added to the rapidly stirred solution under nitrogen. After stirring for 6 hours, the reaction was quenched with 3 ml of triethylamine. The reaction mixture was washed with a saturated solution of Na_2CO_3 in water (100 ml, 3 times), and brine (100 ml, 1 time), and dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure to obtain the viscous pale yellow liquid which solidifies upon standing at room temperature; the yield was quantitative. The product 1,9-dimethyl-5-mesityldipyrromethane was used without further purification.

A solution of 1,9-dimethyl-5-mesityldipyrromethane in 250 ml freshly distilled tetrahydrofuran (THF) was prepared, and a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (7.02 g, 30.9 mmol) in 35 ml of THF was added slowly to the stirred solution under nitrogen. After stirring for 1 hour, the reaction was quenched with 10 ml of triethylamine. The solvent was removed under reduced pressure. The product mixture was dissolved in 500 ml of dichloromethane, and the solution was washed with saturated $NaHCO_3$ solution (250 ml, 3 times) and brine (250 ml, 1 time). The solution was then dried over anhydrous Na_2SO_4 and filtered. The product 1,9-dimethyl-5-mesityldipyrromethene was used for the next step without further purification.

A solution of zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$) (20 g, 91 mmol) in 100 ml of methanol was added to the solution of 1,9-dimethyl-5-mesityldipyrromethene in dichloromethane under air. The reaction mixture was stirred overnight. After that, the reaction mixture was filtered using filter paper, and the

solvents were removed under reduced pressure yielding a dark red solid. The obtained solid was passed through a short neutral alumina plug using hexanes/dichloromethane (7/3) mixture as eluent; the orange-red portion was collected. The solvents were removed, and the solid was recrystallized from CH_2Cl_2/MeOH, yielding 2.5 g of dark green solid *zDIP2* (12.3 % total yield). The obtained *zDIP2* product was further purified by sublimation under high vacuum (10^{-5} torr) using gradient temperature zones of 220 °C/160 °C/120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.92 (s, 4H), 6.46-6.43 (m, *J* = 4.25 Hz, 4H), 6.13 (d, *J* = 3.94 Hz, 4H), 2.37 (s, 6H), 2.14 (s, 12H), 2.11 (s, 12H) matches well with published data.[50]

Bis(1,3,7,9-tetramethyl-5-mesityldipyrrinato) zinc (zDIP3). 3.0 g of orange-red solid (13 % total yield). The obtained *zDIP3* was further purified by sublimation under high vacuum (10^{-5} torr) using 230 °C/160 °C/120 °C gradient temperature zones. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 6.93 (s, 4H), 5.91 (s, 4H), 2.35 (s, 6H), 2.12 (s, 12H), 2.04 (s, 12H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 155.90, 143.63, 143.15, 137.35, 136.22, 135.57, 134.54, 128.73, 119.56, 21.21, 19.26, 16.12, 14.83. HSMS: calcd for $C_{44}H_{51}N_4Zn$ (MH^+): 699.3400, found: 699.3407. C, H, N elemental analysis for $C_{44}H_{51}N_4Zn$: calcd (%) C (75.47), H (7.20), N (8.00); found (%) C (75.84), H (7.27), N (8.06).

Bis(2,8-diethyl-1,3,7,9-tetramethyl-5-mesityldipyrrinato) zinc (zDIP4). 0.8 g of orange-red solid (8 % total yield). The obtained *zDIP4* was further purified by sublimation under high vacuum (10^{-5} torr) using 250 °C/160 °C/120 °C gradient temperature zones. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 6.92 (s, 4H), 2.36 (s, 6H), 2.25 (q, *J* = 7.40 Hz, 8H), 2.11 (s, 12H), 1.97 (s, 12H), 1.19 (s, 12H), 0.91 (t, *J* = 7.49 Hz, 12H). ^{13}C NMR (500 MHz, $CDCl_3$): δ ppm 154.68, 142.03, 137.19, 137.10, 137.03, 136.00, 134.17, 130.66, 128.55, 21.24, 19.47, 17.92, 15.25, 14.35, 11.75. HSMS: calcd for $C_{52}H_{67}N_4Zn$ (MH^+) 811.4652, found 811.4658. CNH analysis for $C_{52}H_{66}N_4Zn$: calcd (%) C (76.87), H (8.19), N (6.90); found C (76.98), H (8.35), N (6.97).

Synthesis of heteroleptic complexes *zDIP2'* and *zDIP3'*. Representative procedure for *zDIP2'* is the following.

Zinc(*1,9-dimethyl-5-mesityldipyrrinato)(2,2,6,6-tetramethyl-3,5-heptanedionato)* (*zDIP2'*). Concentrated HCl (4 drops) was added to a solution of *zDIP2* (96 mg, 0.149 mmol) in 15 ml dichloromethane. The reaction mixture was rigorously shaken for 30 seconds, then washed with brine (2 times), and Na_2CO_3 solution (2 times). The obtained solution of ligand in dichloromethane was dried over anhydrous Na_2CO_3 and filtered. The dried dipyrrin ligand was used without further purification.

A solution of bis-(2,2,6,6-tetramethyl-3,5-heptanedionato)zinc, $Zn(dpm)_2$ (150 mg, 0.347 mmol) in a mixture of dichloromethane/methanol (40/40 ml) was prepared, and slowly added to a solution of the dipyrrin ligand in 15 ml dichloromethane over the course of 5 minutes while stirring. The reaction mixture became brightly emissive upon addition of $Zn(dpm)_2$. To prevent disproportionation of *zDIP2'*, the solvents were immediately removed under reduced pressure after addition of $Zn(dpm)_2$, yielding an orange red solid. The obtained orange solid was dissolved in 10 ml dichloromethane, and 15 ml of methanol was layered on top. This solution was stored for 2 days at -5 °C. Two distinct types of red crystals were subsequently formed; large orange red crystals (heteroleptic complex) and small cubic dark red crystals (homoleptic complex). The large orange red crystals were manually separated under a microscope, yielding 18 mg (9.6%) of heteroleptic complex *zDIP2'*. The obtained crystals were suitable for crystal structure determination by X-ray diffraction. Unlike the homoleptic complex *zDIP2*, the heteroleptic product *zDIP2'* is highly emissive in dichloromethane under UV-lamp illumination. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.89 (s, 2H), 6.42–6.35 (m, 2H), 6.15–6.10 (m, 2H), 5.83-5.80 (m, 1H), 2.35 (s, 3H), 2.23 (s, 6H), 2.14 (s, 6H), 1.19 (s, 18H). ^{13}C NMR (400 MHz, CDCl3, ppm): 203.52, 158.63, 143.85, 138.78, 136.86, 136.81, 135.34, 131.87, 127.41, 116.86, 89.60, 41.73, 28.40, 21.09, 20.06, 16.79. HSMS: calcd for $C_{31}H_{41}N_2O_2Zn$ (MH^+): 537.2454, found: 527.2463.

Zinc(*1,3,7,9-tetramethyl-5-mesityldipyrrinato)(2,2,6,6-tetramethyl-3,5-heptanedionato)* (*zDIP3'*). *zDIP3'* was synthesized using a procedure similar to that used to prepare *zDIP2'*. An orange solid mixture of heteroleptic and homoleptic complexes was obtained. Unlike the weakly emissive solid of other zinc dipyrrins, this orange solid mixture has very bright yellow emission under UV-illumination. The

heteroleptic complex was separated from the homoleptic one by sublimation under high vacuum (10^{-5} torr) using 170 °C/120 °C/50 °C gradient temperature zones (note that *zDIP3* sublimes at the higher temperature of 230 °C, see above), yielding of *zDIP3'* (50% yield). A suitable crystal from the sublimed solid was used for crystal structure determination. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.91 (s, 2H), 5.92 (s, 2H), 5.79 (s, 1H), 2.33 (s, 3H), 2.13 (s, 12H), 1.28 (s, 6H), 1.18 (s, 18H). ^{13}C NMR (400 MHz, CDCl3, ppm): 203.25, 155.90, 144.19, 144.06, 137.46, 135.83, 135.71, 134.87, 128.75, 119.62, 89.46, 41.65, 28.38, 21.19, 19.68, 16.48, 14.81. HSMS: calcd for $C_{33}H_{45}N_2O_2Zn$ (MH^+): 565.2767, found: 565.2764.

Global Analysis of femtosecond Transient Absorption Spectra:

The transient absorption spectra of *zDIP1-3* indicate that compared to *zDIP1*, the population from initially formed S_1 state evolves faster to CT state for both *zDIP2* and *zDIP3*. In addition, the rate for formation of CT state and its subsequent relaxation were found to be dependent on the polarity of the surrounding medium. To quantify the rate of decay of these states in different polarity solvents, TA spectra were fit with a linear decomposition model described elsewhere in detail.[1] In brief, the signal can be described by:

$$S(\lambda, t) = \sum_n C_n(t)\sigma_n(\lambda) \qquad \text{(S1)}$$

where the time dependent TA signal, $S(\lambda,t)$, can be decomposed into a set of time independent species associated difference spectra (SADS), $\sigma_n(\lambda)$, and time dependent amplitudes, $c_n(t)$. Each SADS corresponds to the characteristic TA spectrum of an excited configuration of the system and consist of both positive features due to excited state absorption and negative features due to stimulated emission and ground state bleach. $c_n(t)$ is calculated assuming that the evolution of the initially excited population is governed by a series of sequential first order rate processes.

The kinetic model described in the main paper (Figure 9) was used to fit all the femtosecond transient absorption spectra. Based on the polarity of the solvents used, they were categorized as

1) nonpolar (cyclohexane), 2) weakly polar (toluene) and 3) polar (dichloromethane and acetonitrile). Depending on the solvent category different transfer matrices, K_{ij} are used for the kinetic model:

Category 1) $K_{ij} = [k_{11}]$, Category 2) $K_{ij} = \begin{bmatrix} k_{11} & k_{21} \\ k_{12} & k_{22} \end{bmatrix}$, Category 3) $K_{ij} = \begin{bmatrix} 0 & 0 \\ k_{12} & k_{22} \end{bmatrix}$

Here k_{11} and k_{22} represent the first order rates for the decay of the S_1 excited state and the CT state, respectively. And k_{12} and k_{21} represent the first order transfer rates from S_1 excited state to the CT state and from the CT state to the S_1 excited state. The solvent polarity dependent data for *zDIP1* (shown in Figure 8) was fitted with this model and the SADS required to model each of the data are shown in Figure S18 (a,c,e,g). These SADS are the characteristic transient spectral signature for the initially populated S1 excited state (σ_1) and subsequently formed CT state (σ_2). The corresponding fits to the time slices of the ground state bleach and CT state induced absorption are also shown in Figure S18 (b,d,f,h).

Excited State Dynamics of *zDIP2* and *zDIP3*:

Figure S19 and S21 shows the solvent polarity dependent TA spectra for *zDIP2* and *zDIP3*, respectively. In cyclohexane, both *zDIP2* (Fig. S19a) and *zDIP3* (Fig. S21a) show similar dynamics to that observed for *zDIP1* in the main paper, however the relaxation of the S_1 excited state to the ground state for *zDIP3* is faster (~ 1.4 ns) compared to *zDIP1* (4.5 ns) and *zDIP2* (4.8 ns). This dramatic decrease in S_1 excited state lifetime for *zDIP3* is also consistent with the TCSPC results (shown in Fig. S23) and it is due to presence of higher non-radiative processes discussed in the main paper (Figure 5).

However in toluene, for both *zDIP2* (Fig. S19b) and *zDIP3* (Fig. S21b) over the time some population from initially formed S_1 state evolve to CT state (indicated by the induced absorption

growing at ~370 nm) and some relax back to the ground state (stimulated emission at ~525 nm remains till 1ns). And so an equilibrium exists between the CT state and S_1 state similar to that observed in *zDIP1* in the main paper. The forward and backward rate constants ($1/k_{CT}$ and $1/k_{CR}$) between the S_1 and the CT states obtained from the global analysis are 8.6 and 15.5 ps; 2.3 and 11.2 ps respectively for *zDIP2* and *zDIP3*. Once formed, the CT state decays with a rate constant ($1/k_{rec}$) of 4.0 ns and 2.5 ns for *zDIP2* and *zDIP3*, respectively. Unlike toluene, in polar solvents such as acetonitrile *zDIP3* (Fig. S21c) evolves to CT state at a faster rate ($1/k_{CT}$ = 1 ps) due to the stabilization of the CT states by the large solvation energy of the acetonitrile. The SADS and the fits for the time traces obtained from the modeling of the TA spectra using global analysis for *zDIP2* and *zDIP3* are shown in Figure S20 and S22, respectively.

Comparison between Spectro-electrochemistry and TA measurements of *zDIP1*:

The spectral assignment of *zDIP1* anion is obtained from spectro-electrochemical reduction experiments in dichloromethane (Figure 7, main paper). This assignment is used to assign the induced absorption band at 517 nm from TA measurements (Figure 8, main paper). In Fig. S25 the two absorption profiles are overlaid to make a direct comparison between the two experiments. Although the peak at 517 nm matches perfectly, the bleach shape looks different between the two experiments. This is mainly due to the presence of an additional peak between 370-470 nm (encircled in green) in the spectro-electrochemical reduction experiments. The absence of this peak in TA data is probably because the molecule forms both a *zDIP1* radical cation and radical anion in its excited state (as probed in TA experiment) whereas in the reduction experiments there is only *zDIP1* radical anion present. We suspect that the total absorptions for the radical anion is obscured by the presence of radical cation, and the anion signal may be overwhelmed by the bleach signal which is doubled due to removal of two chromophores (one

forming the anion and the other forming the cation). Another possible reason could be a two electron reduction, *i.e.* reduction of both dipyrrin ligands, in spectro-electrochemical experiments.

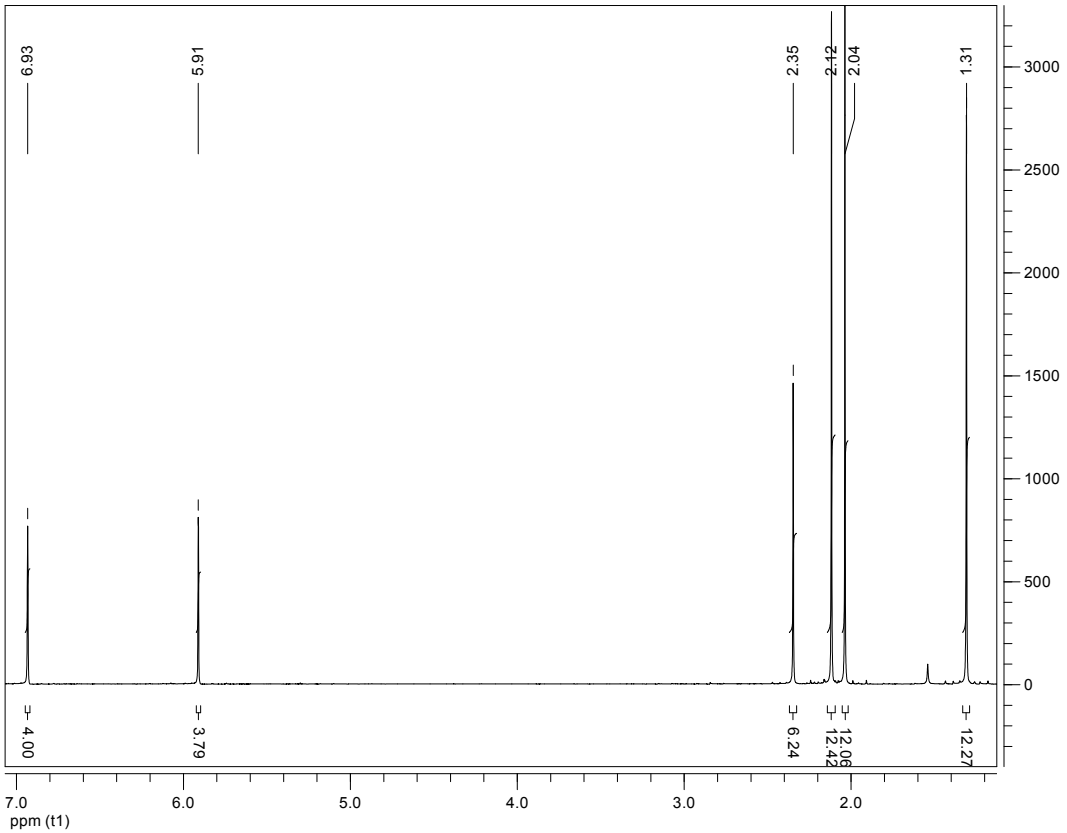


Figure S1. ^{1}H NMR of *zDIP3*.

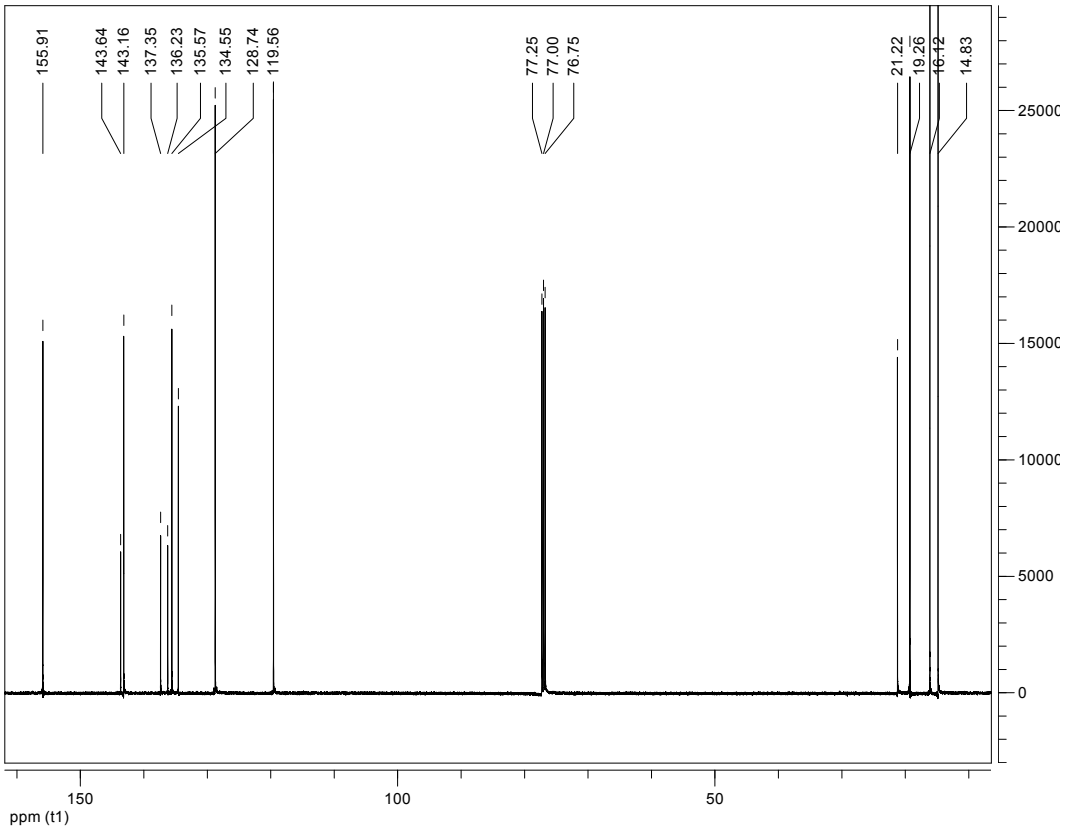


Figure S2. ^{13}C NMR of *zDIP3*.

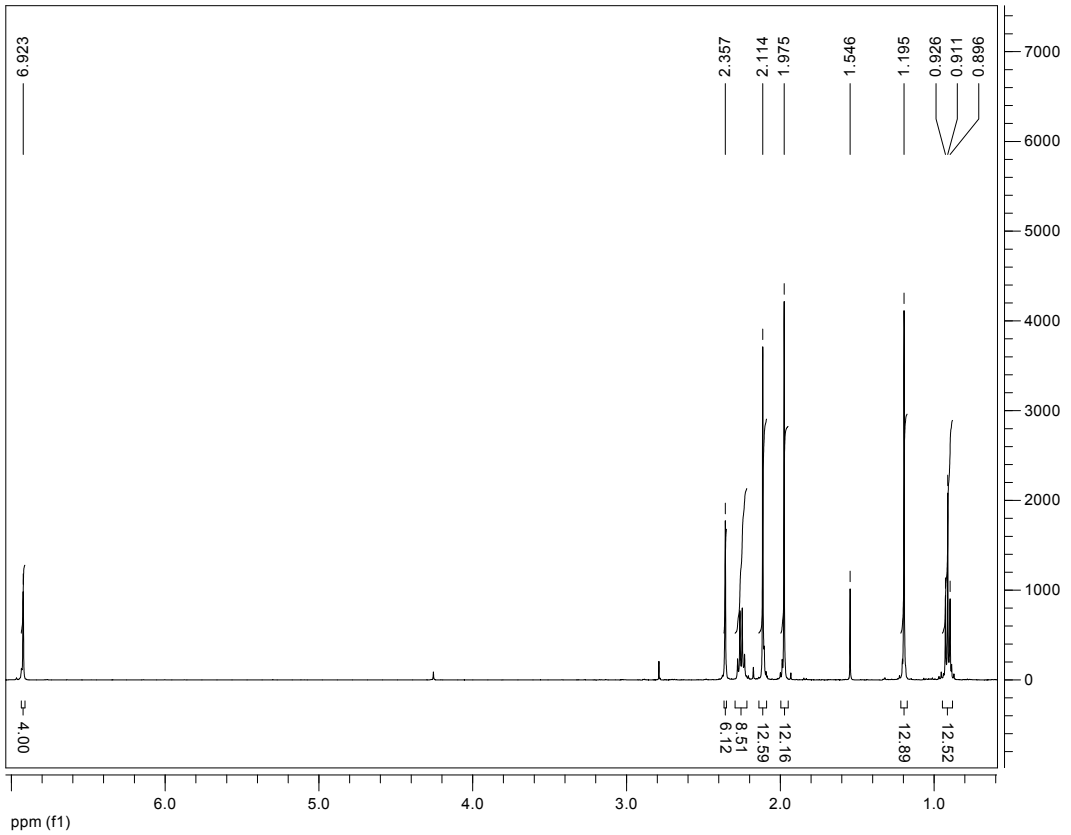


Figure S3. ^{1}H NMR of *zDIP4*.

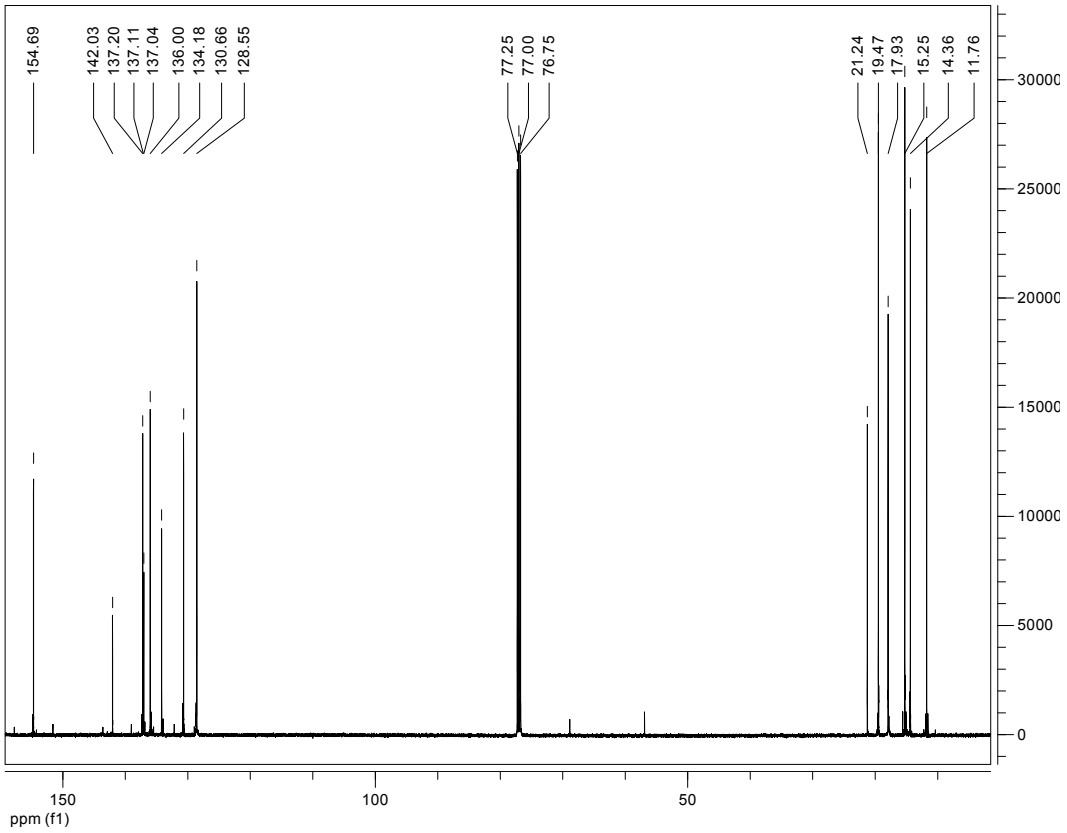
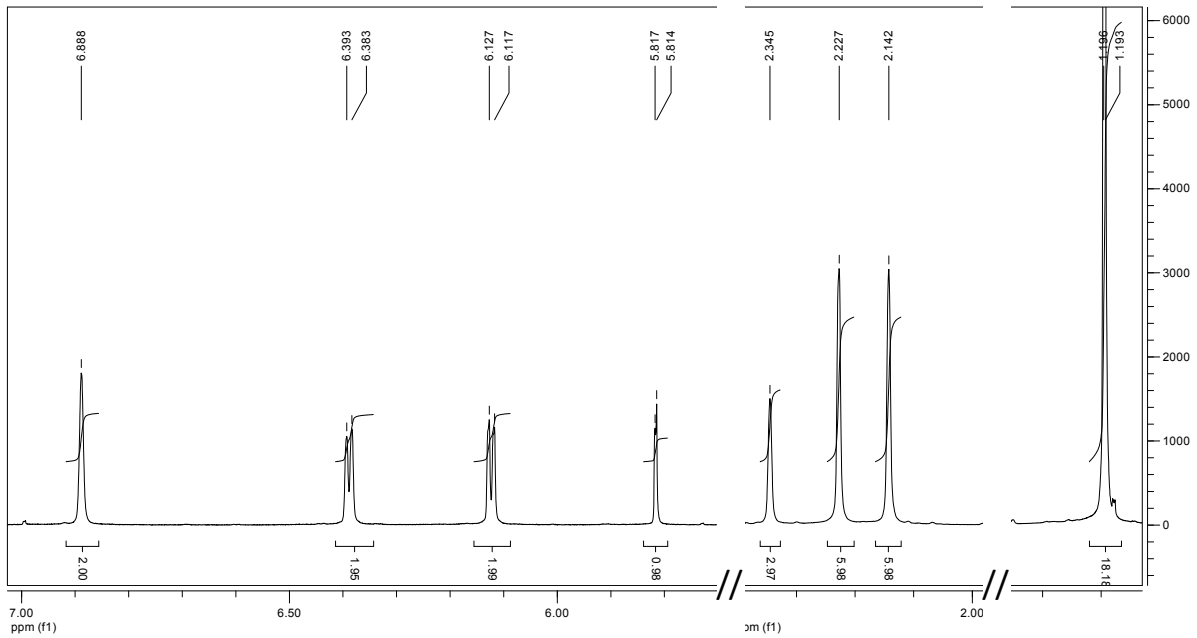


Figure S4. ^{13}C NMR of *zDIP4*

a)



b)

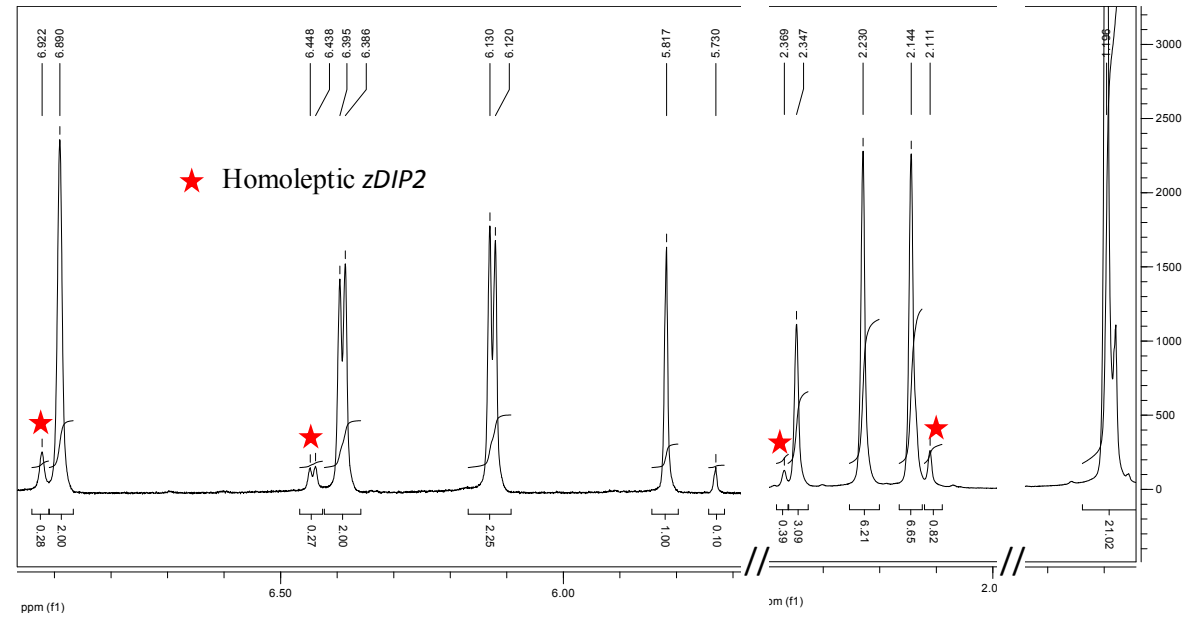


Figure S5. ^{1}H NMR of *zDIP5* in $CDCl_3$ over time. (a) freshly prepared solution of *zDIP5* and (b) solution in NRM tube after 4 hours, estimated molar ratio of heteroleptic:homoleptic complexes (*zDIP5*: *zDIP2* = 15:1)

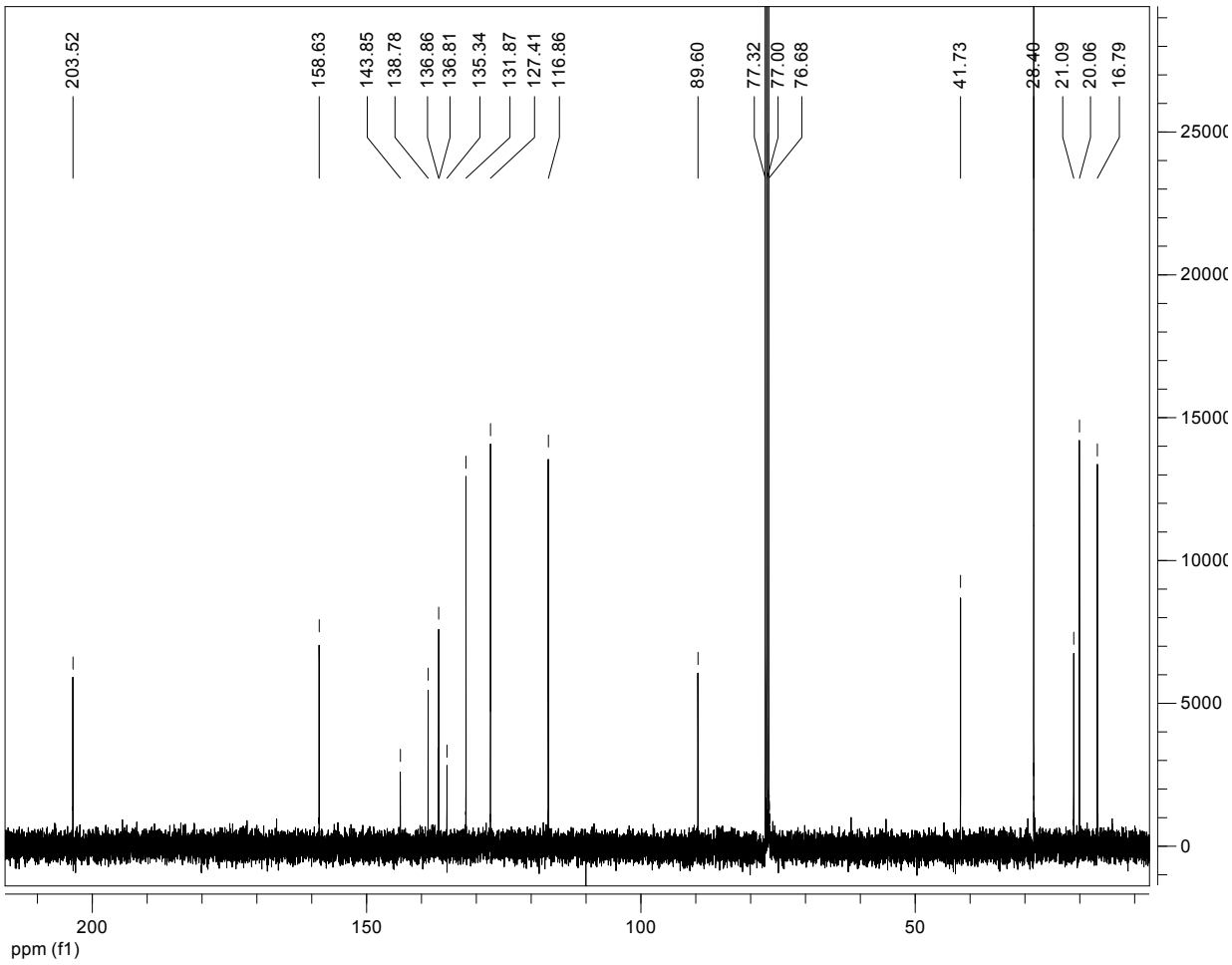
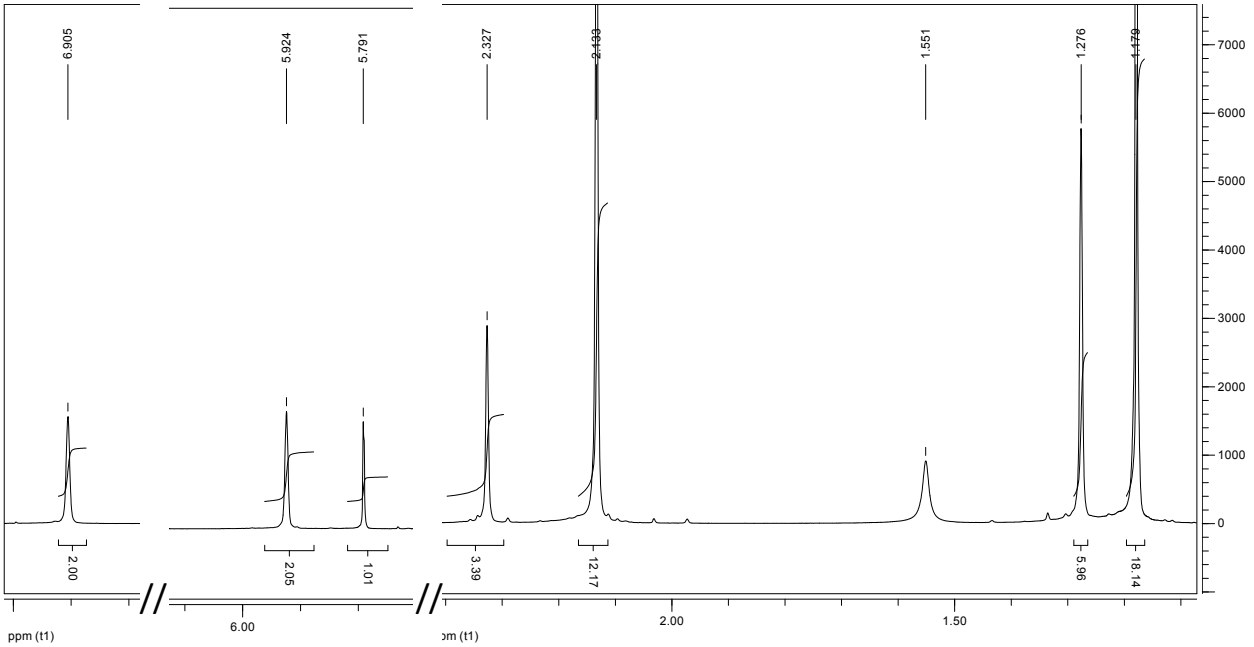


Figure S6. ^{13}C NMR of *zDIP5* in $CDCl_3$.

a)



b)

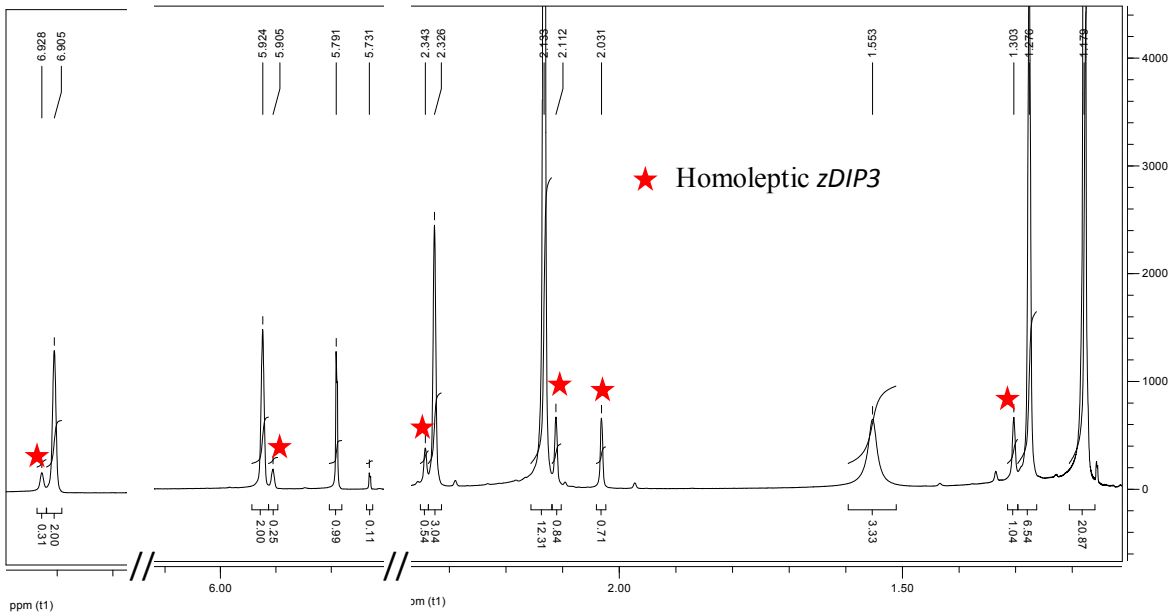


Figure S7. ^{1}H NMR of *zDIP6* in $CDCl_3$ over time. (a) freshly prepared solution of *zDIP6* and (b) solution in NRM tube after 8 hours, estimated molar ratio of heteroleptic:homoleptic complexes (*zDIP6: zDIP3* = 13:1)

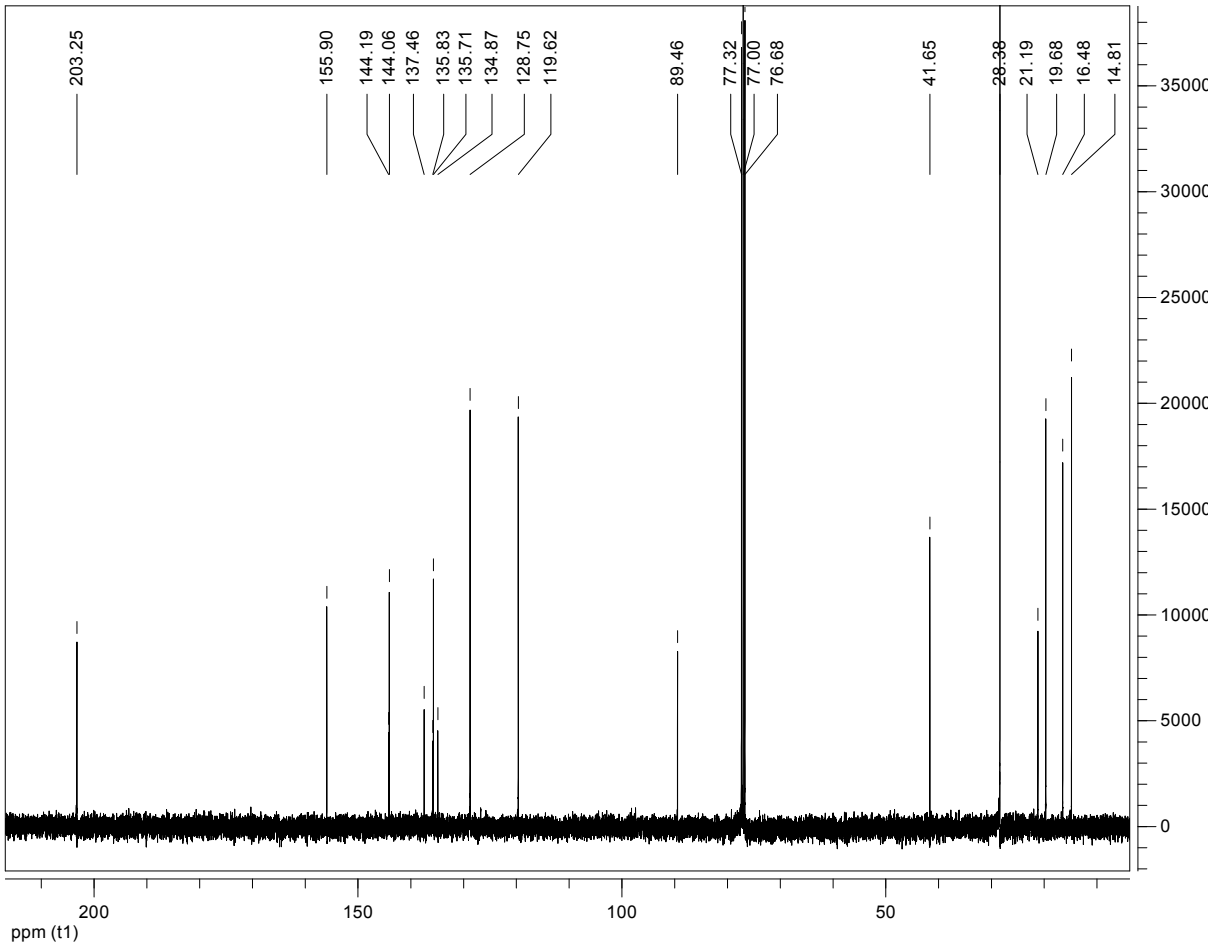


Figure S8. ^{13}C NMR of *zDIP6* in $CDCl_3$.

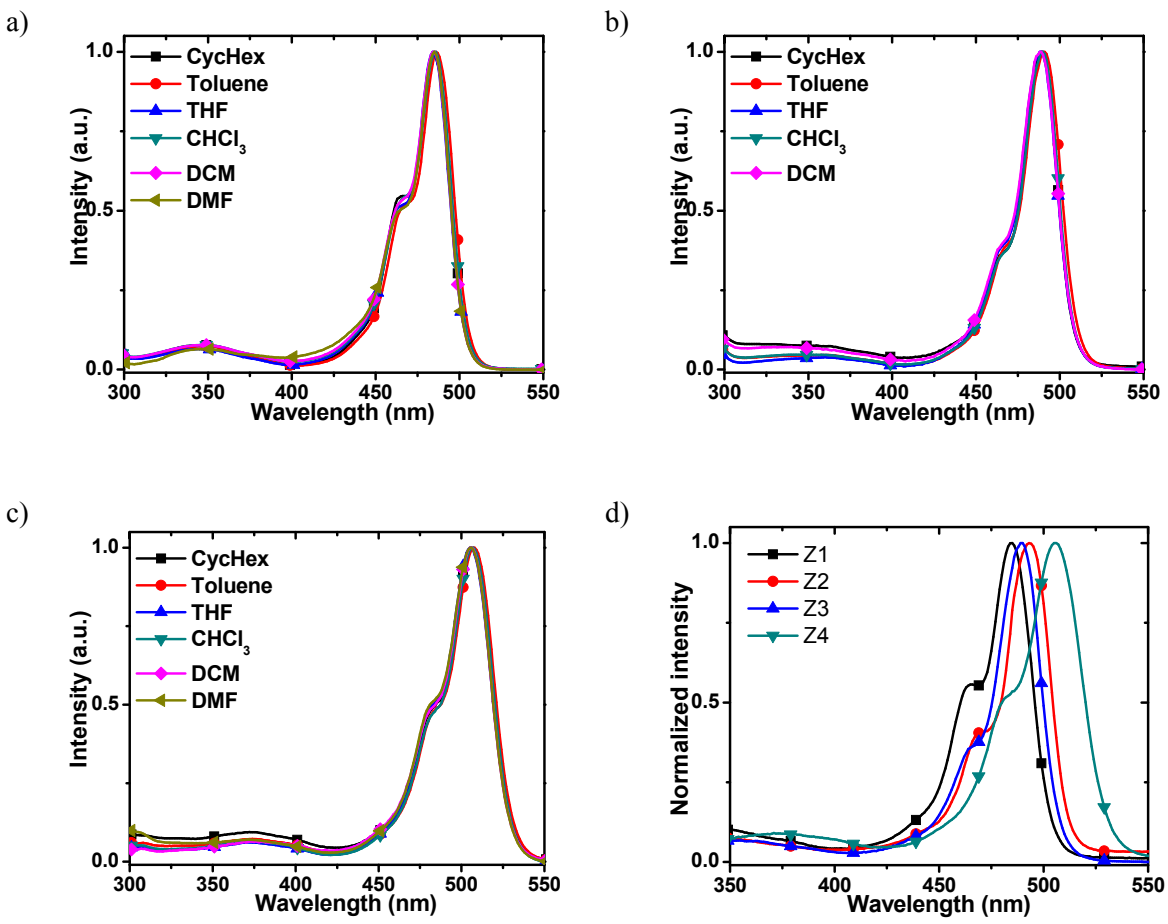


Figure S9. Absorption spectra in different solvents of (a) *zDIP1*, (b) *zDIP3*, (c) *zDIP4*; and (d) absorption spectra of *zDIP1-4* in cyclohexane.

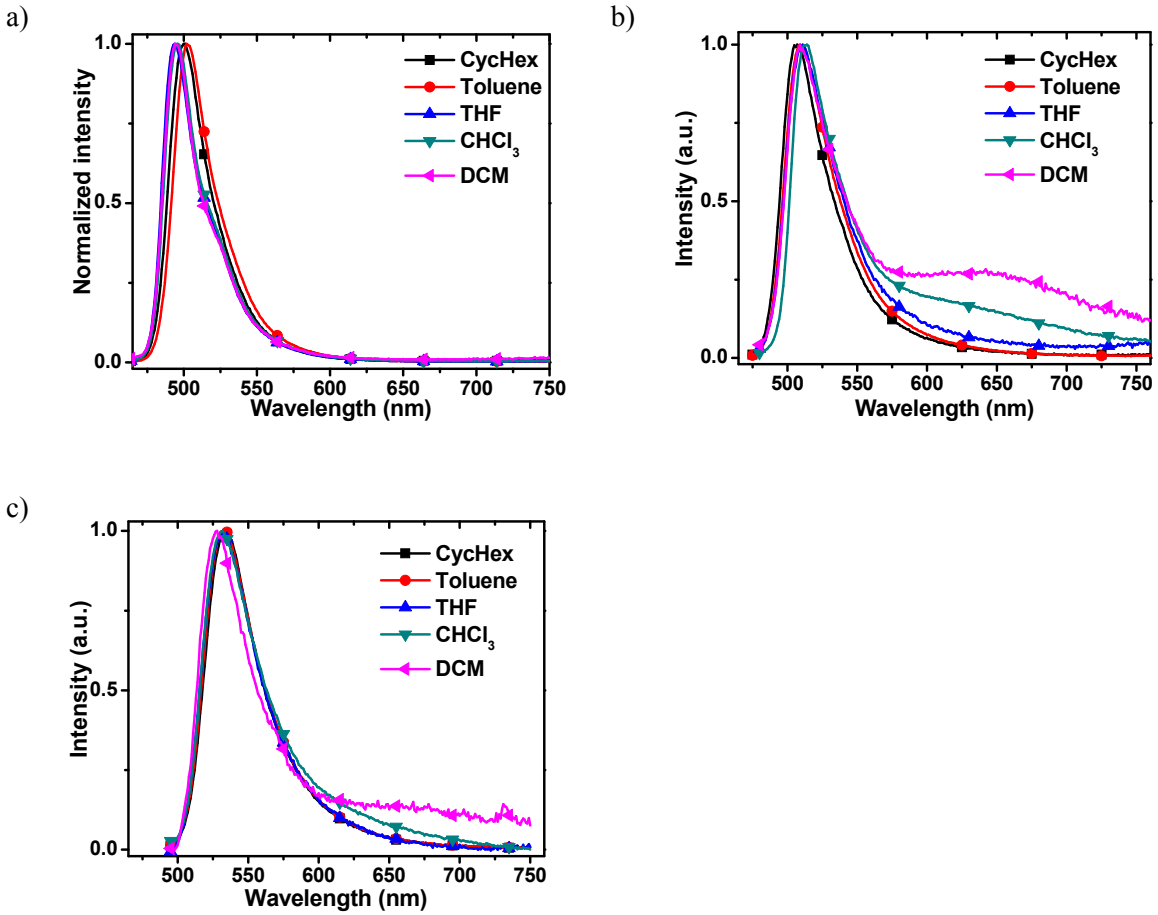


Figure S10. Normalized emission spectra in different solvents of (a) *zDIP1*, (b) *zDIP3* and (c) *zDIP4*.

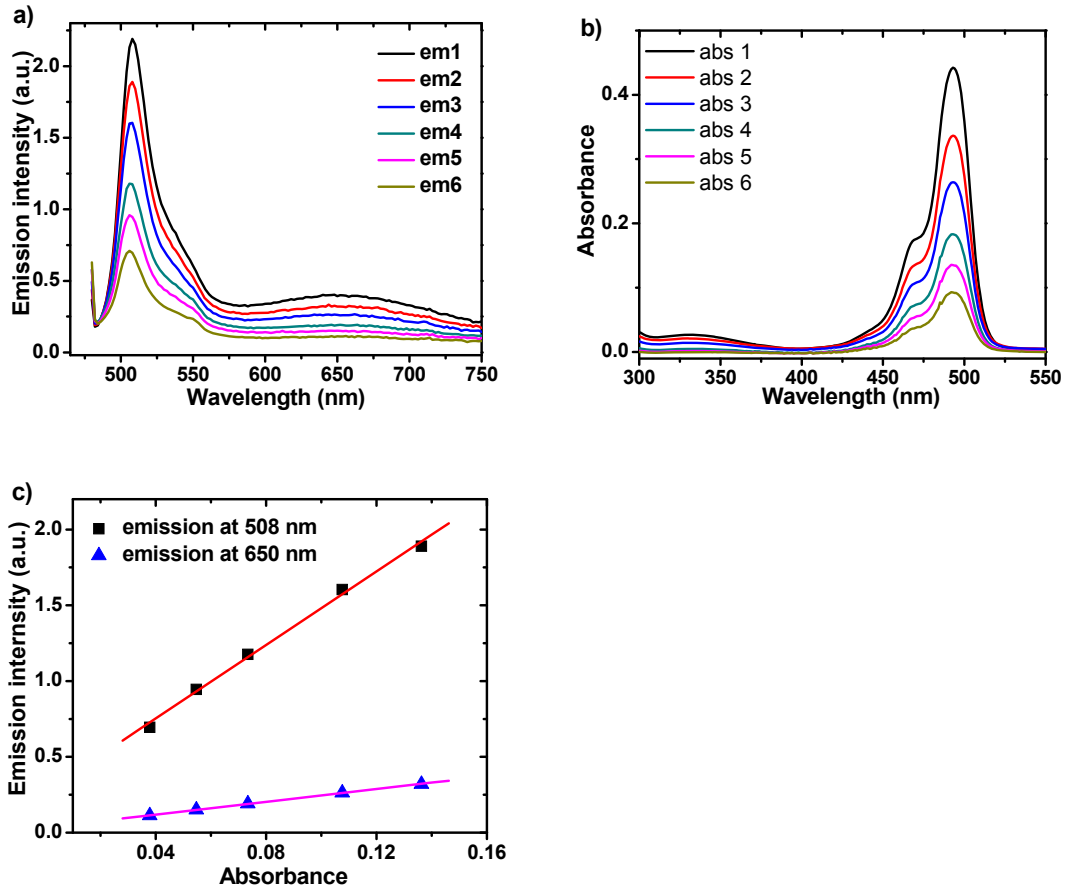


Figure S11. Emission and absorption intensities of *zDIP2* solution in dichloromethane at various concentrations. (a) emission spectra and (b) corresponding absorption spectra as concentration decreases; (c) emission intensities are plotted vs. absorption intensity, linear dependence of emission peaks at 508 and 650 nm excludes excimer formation in solution.

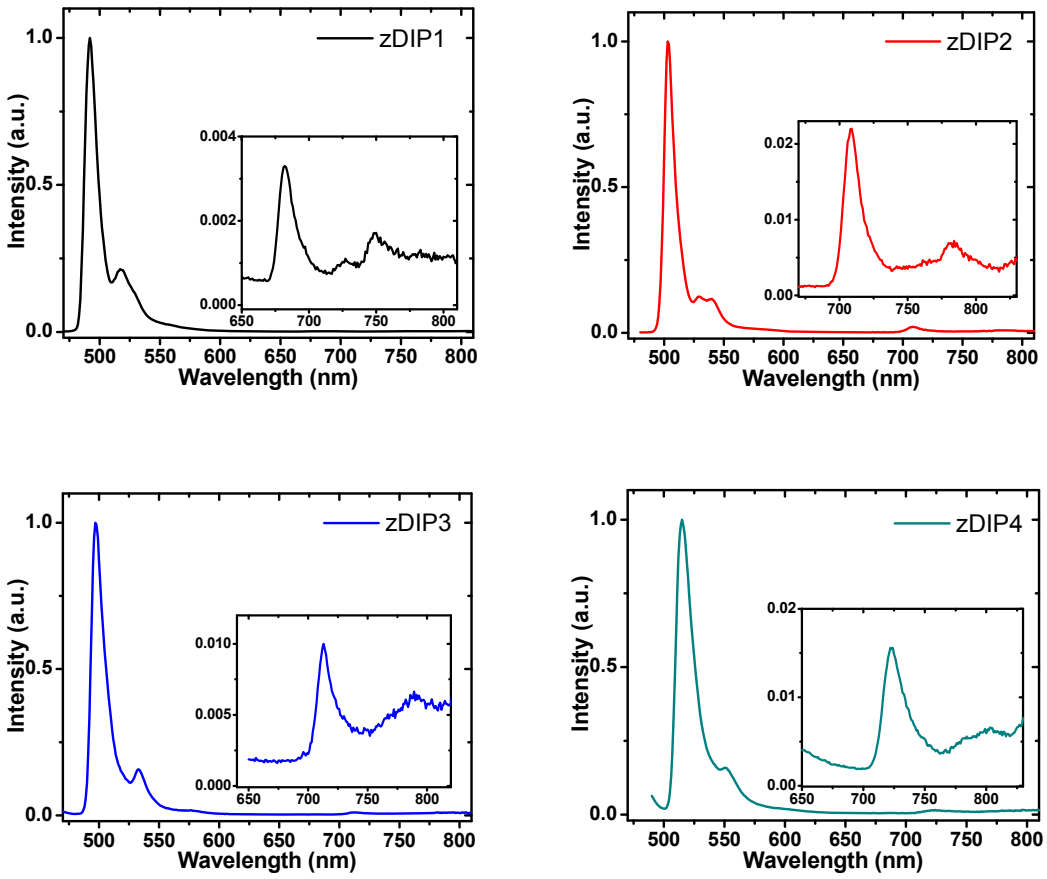


Figure S12. Emission spectra of *zDIP1-4* in 2-methyl tetrahydrofuran at 77K.

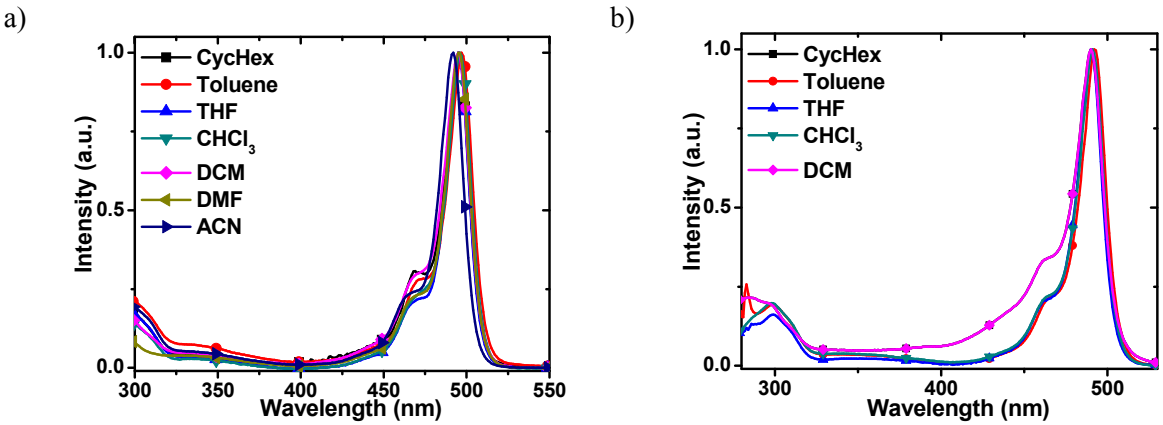


Figure S13. Absorption spectra of heteroleptic complexes (a) *zDIP5* and (b) *zDIP6* in different solvents.

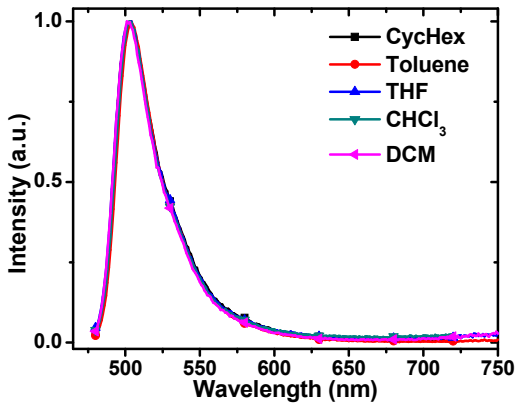


Figure S14. Emission spectra of *zDIP6* in different solvents.

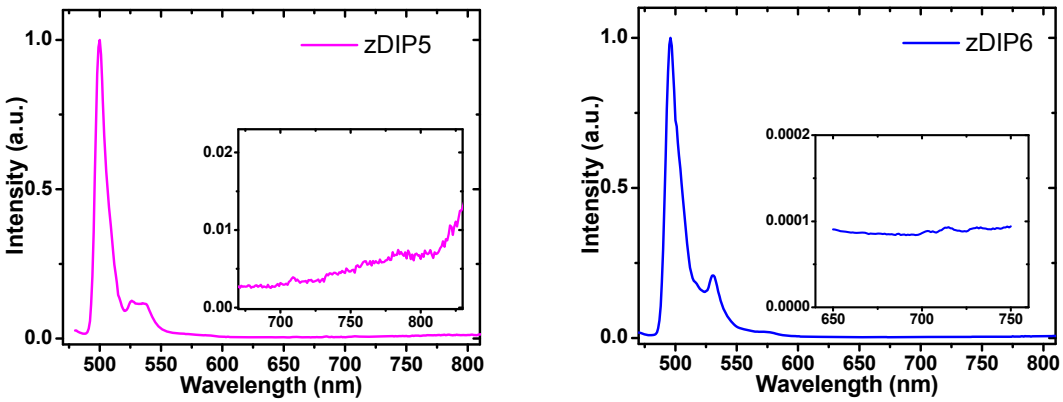


Figure S15. Emission spectra of *zDIP5* (left) and *zDIP6* (right) in 2-methyl tetrahydrofuran at 77K.

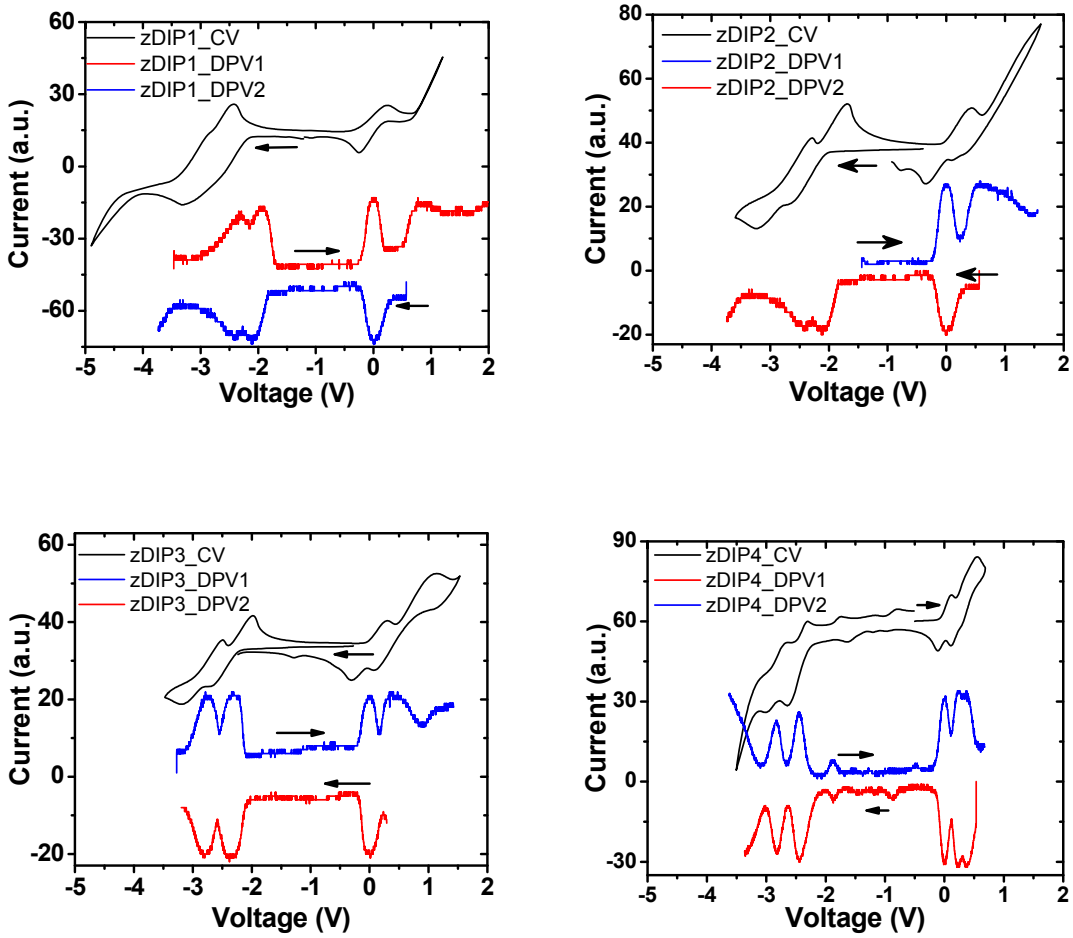


Figure S16. Electrochemical measurements of *zDIP1-4* in dry THF under N_2, scan rate is 100 mV/s. Fc^+/Fc was used as internal standard.

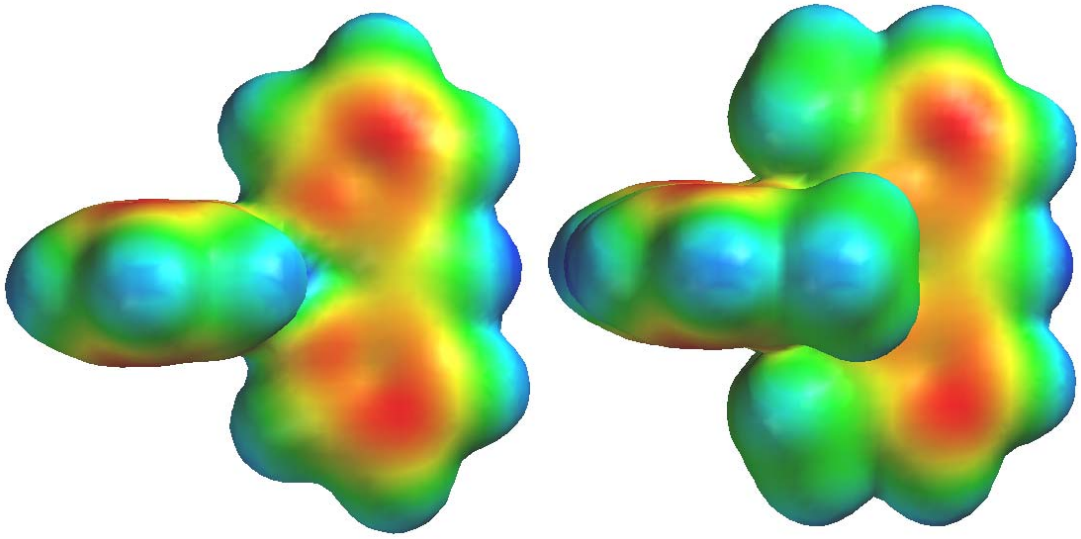


Figure S17. Electron density surfaces of *zDIP1* (left) and *zDIP2* (right) with D2d symmetry, performed at B3LYP/LACVP** level of theory. Mesityl group are omitted for simplicity of calculation.

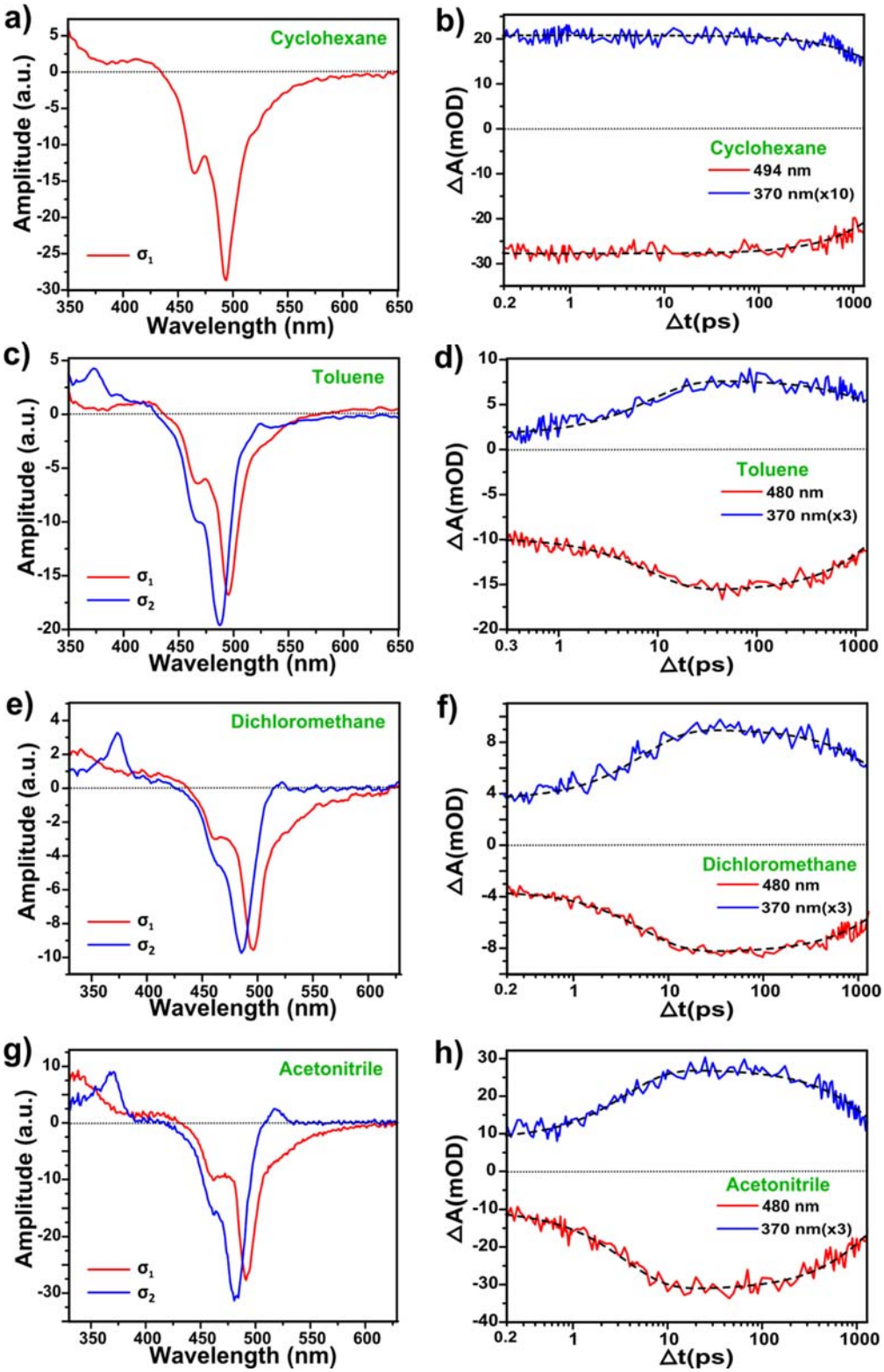


Figure S18: (a, c, e, g) SADS used to model the transient spectra of *zDIP1*. (b, d, f, h) The fits (black dashed) based on SADS analysis for the time slices taken through the ground state bleach (red) and spectral range indicative of CT state (blue).

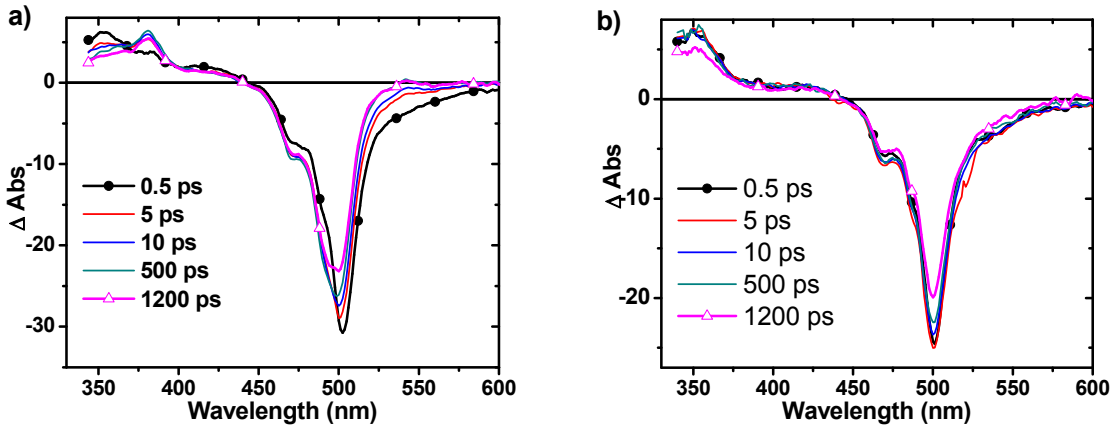


Figure S19. Transient absorption spectra of z*DIP2* in (a) toluene and (b) cyclohexane.

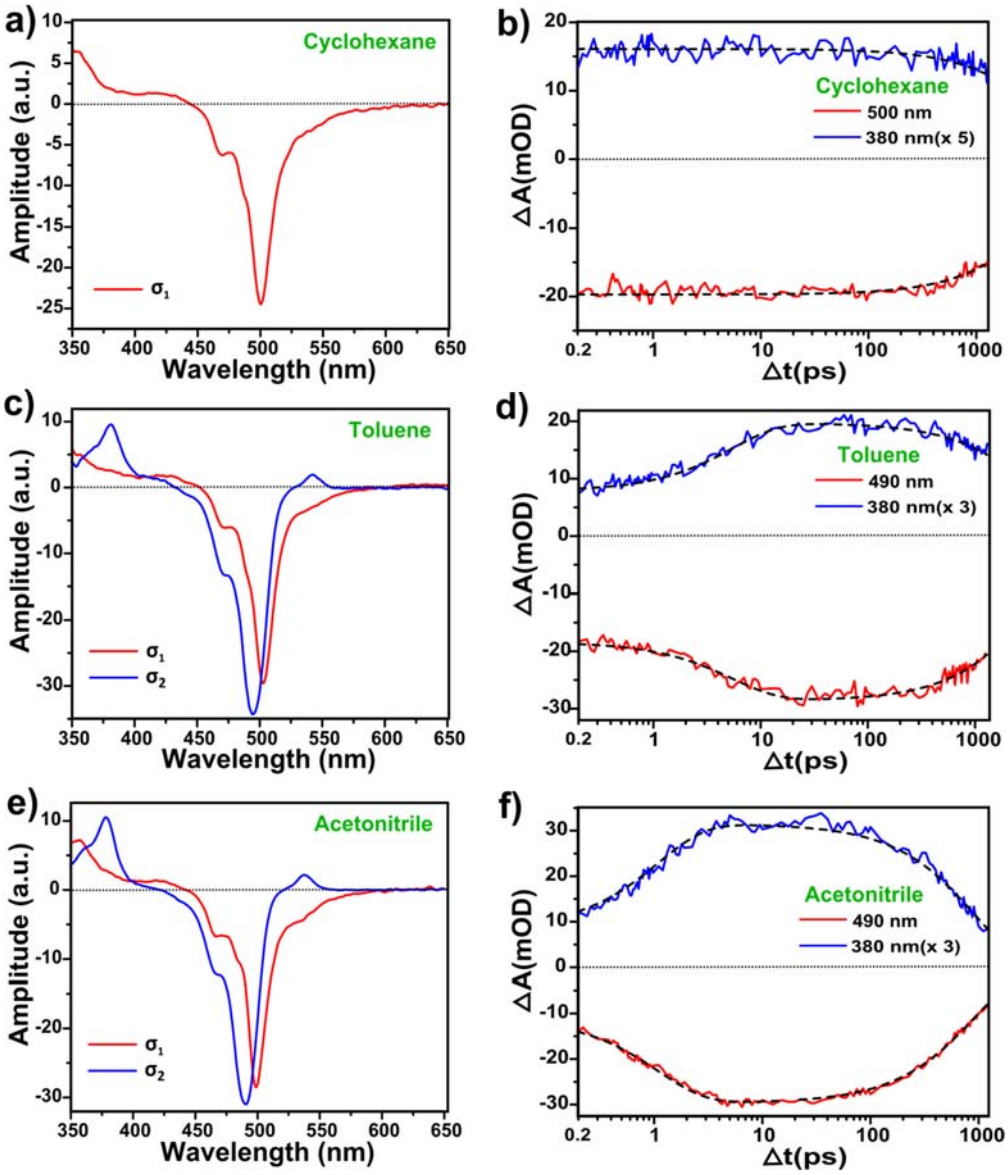


Figure S20: (a, c, e) SADS used to model the transient spectra of *zDIP2*. (b, d, f) The fits (black dashed) based on SADS analysis for the time slices taken through the ground state bleach (red) and spectral range indicative of CT state (blue).

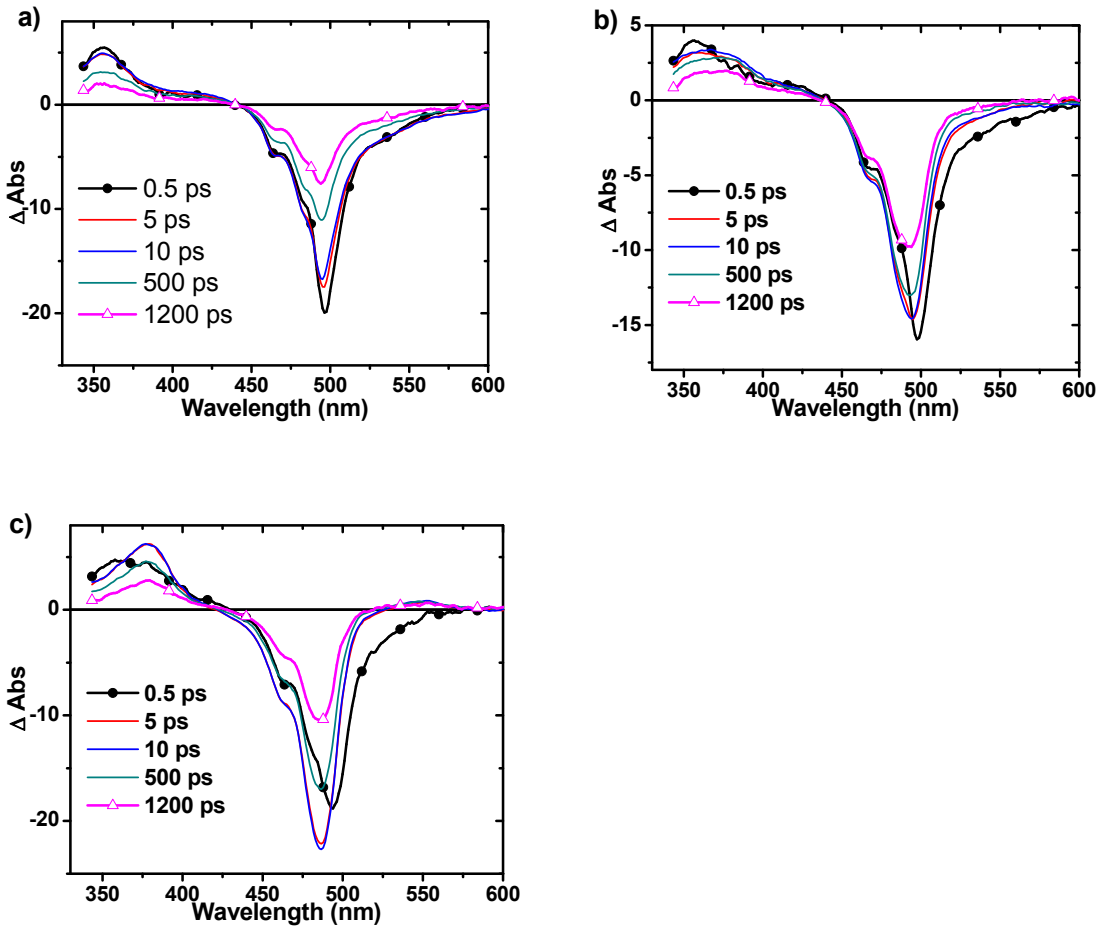


Figure S21. Transient absorption spectra of *zDIP3* in (a) Cyclohexane, (b) toluene and (c) acetonitrile.

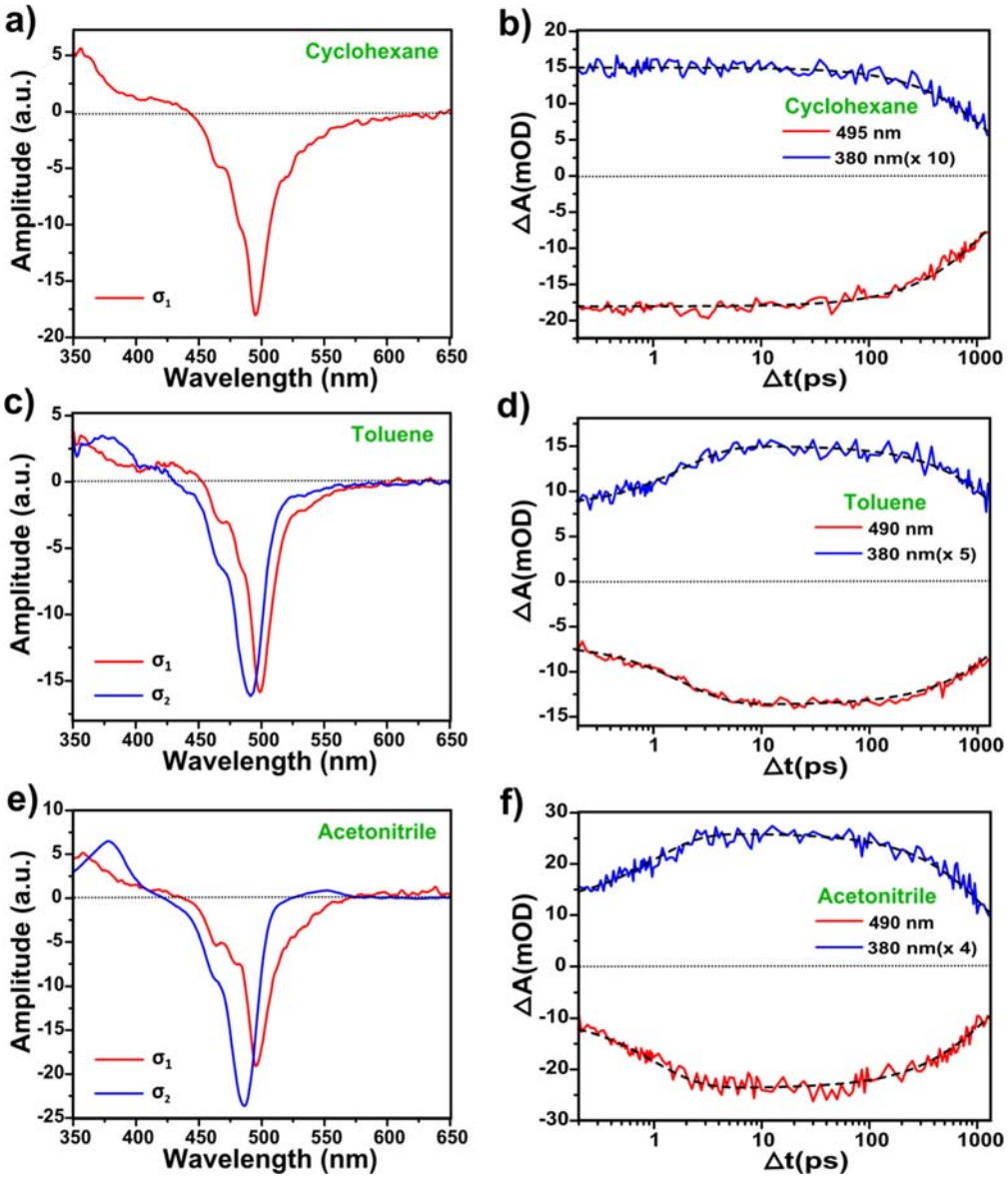


Figure S22: (a, c, e) SADS used to model the transient spectra of *zDIP3*. (b, d, f) The fits (black dashed) based on SADS analysis for the time slices taken through the ground state bleach (red) and spectral range indicative of CT state (blue).

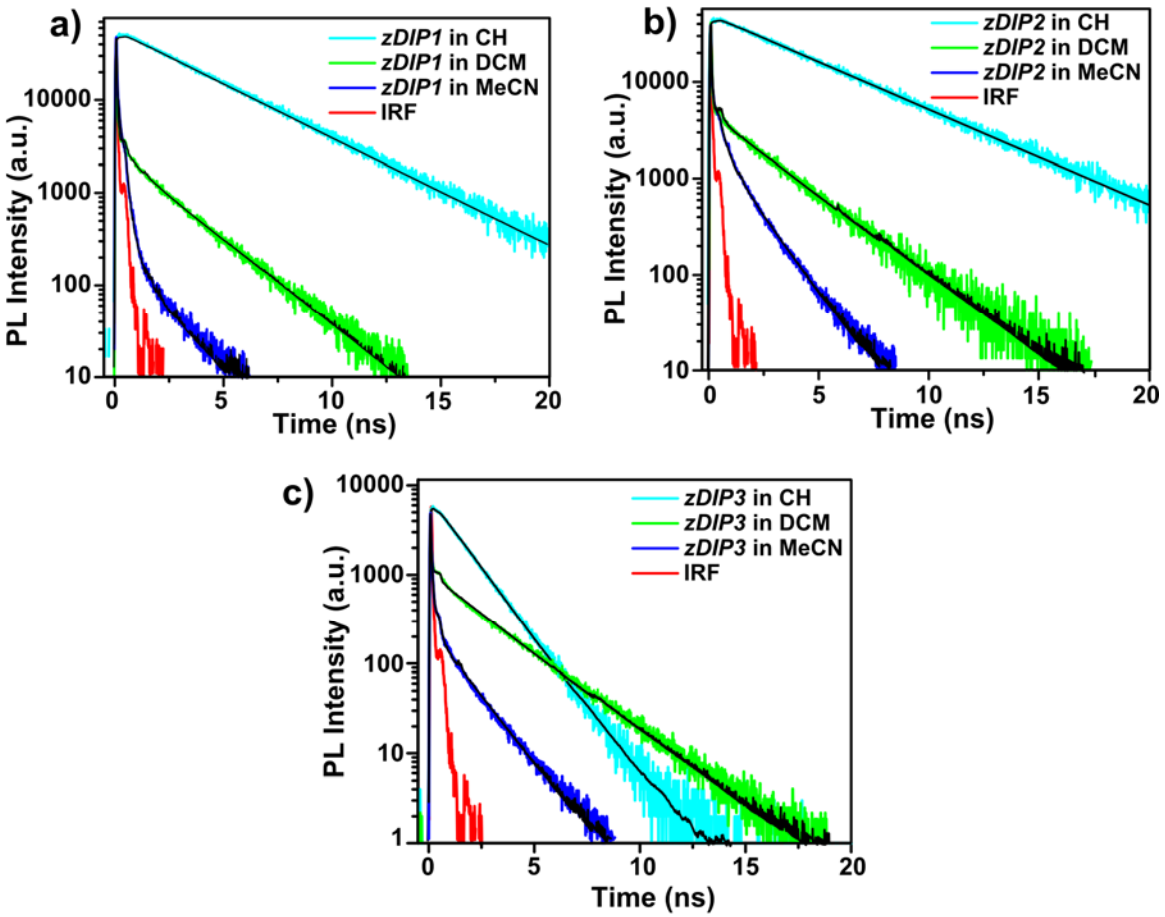


Figure S23: Normalized photoluminescence (PL) measurements of a) *zDIP1*, b) *zDIP2* and c) *zDIP3* in various polarity solvents. The emission is collected at 520 nm following excitation with 500 nm. The instrument response function (FWHM ~ 22 ps) is also shown in red. The black lines are the fit to the PL measurements with exponential(s) (amplitudes and time constants are shown in table S14).

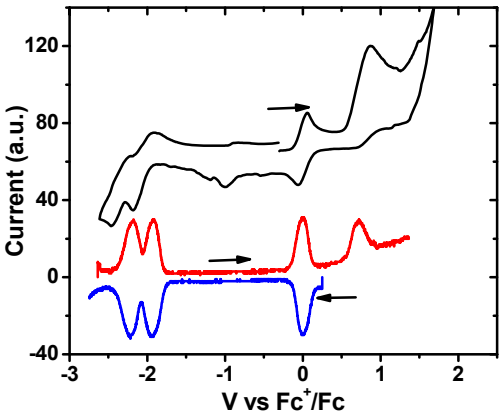


Figure S24. Electrochemical measurement of *zDIP1* in DCM, *zDIP1* undergoes irreversible oxidation and two reversible reductions.

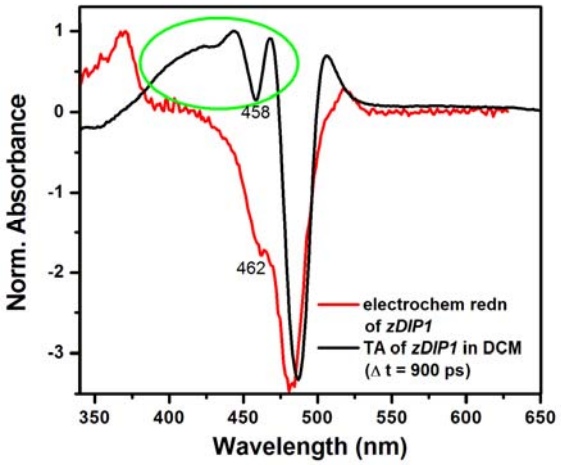


Figure S25. Spectral lineshape comparison between spectro-electrochemical reduction and TA experiments on *zDIP1* in DCM. The encircled portion in green shows the peak responsible for the difference.

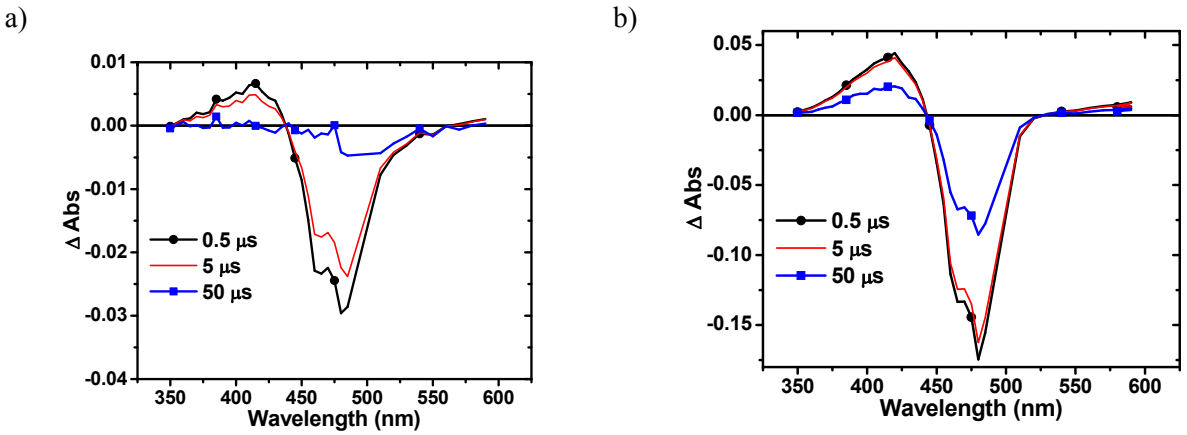


Figure S25. Microsecond transient absorption spectra of *zDIP1* (a) in cyclohexane and (b) in toluene

a) b)

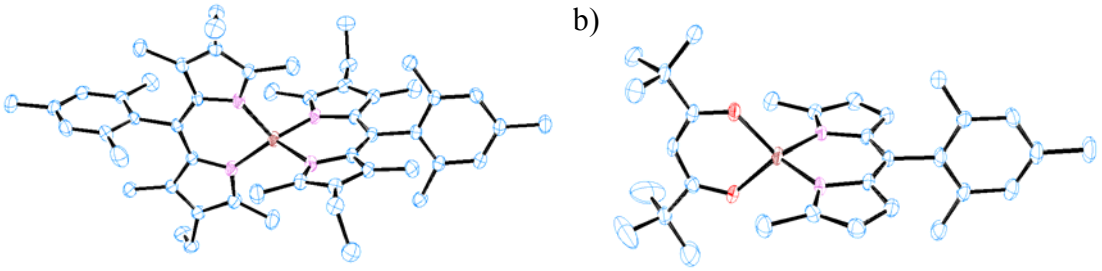


Figure S26. ORTEP diagrams of (a) *zDIP4* and (b) *zDIP5* at 50% probability level. H atoms are omitted for clarity.

Table S1. Photophysical properties of homoleptic and heteroleptic zinc dipyrrin complexes in different solvents at room temperature.

	Solvents	λ_{abs} (max/nm)	$fwhm_{ab}$ (cm^{-1})	λ_{em} (max/nm)	$fwhm_{em}$ (cm^{-1})	$\Delta\nu_{ab-em}$ (cm^{-1})	QE (%)	τ (ns)	k_r (ns^{-1})	k_{nr} (ns^{-1})
zDIP1	CycHex	484	1530	501	1260	638	46.5	4.3	0.11	0.12
	Toluene	486	1443	503	1256	659	33.3	3.0	0.11	0.22
	THF	484	1437	494	1231	406	2.7	2.6[(a)]	0.01	0.37
	$CHCl_3$	485	1483	496	1218	426	2.2	-	-	-
	DCM	485	1471	495	1131	429	1.7	2.1 [(b)]	-	-
	ACN	481	1423	490	1180	396	< 0.1	1.7 [(b)]	-	-
zDIP2	CycHex	493	983	506	944	501	66.0	4.8	0.14	0.07
	Toluene	495	1022	509	959	567	19.0	3.9	0.05	0.21
	THF	493	1016	507	1013	586	0.9	2.9[(a)]	0.003	0.34
	$CHCl_3$	494	1083	509	1013	592	0.5	-[(a)]	-	-
	DCM	493	1074	508 (650)	1108	706	< 0.1	2.5[(b)] (2.2[(c)])	-	-
	ACN	490	1056	508	1494	736	-	1.4 [(b)]	-	-
zDIP3	CycHex	489	1036	507	1500	676	16.3	1.5	0.11	0.56
	Toluene	491	1102	509	1523	736	13.8	2.1	0.07	0.41
	THF	489	1092	511	1576	902	2.0	2.8 [(a)]	0.007	0.35
	$CHCl_3$	490	1057	513	1494	915	0.5	-	-	-
	DCM	488	1127	509 (653)	1591	819	< 0.1	2.4[(b)] (2.5[(c)])	-	-
zDIP4	CycHex	506	1393	533	1480	1026	17.4	1.9	0.09	0.43
	Toluene	508	1323	533	1565	920	13.4	2.4	0.06	0.36

	THF	505	1432	532	1604	982	2.6	2.6[(a)]	0.01	0.37
	$CHCl_3$	507	1296	532	1632	917	0.7	-	-	-
	DCM	506	1403	528 (674)	1503	831	< 0.1	-	-	-
zDIP5	CycHex	495	733	503	863	305	51.6	3.4	0.15	0.14
	Toluene	497	739	506	861	350	48.4	2.8	0.17	0.18
	THF	495	675	504	849	337	41.2	2.3	0.18	0.26
	$CHCl_3$	496	714	505	866	343	42.2	2.2	0.19	0.26
	DCM	495	777	505	885	388	30.3	1.8	0.17	0.39
	DMF	495	781	505	882	386	26.0	-[(a)]	-	-
	ACN	492	713	501	885	367	17.3	-[(a)]	-	-
zDIP6	CycHex	491	757	503	1311	467	8.5	0.8	0.11	1.14
	Toluene	493	739	504	1240	463	8.5	0.8	0.11	1.14
	THF	490	723	503	1290	516	4.9	-[(a)]	-	-
	$CHCl_3$	491	755	503	1220	485	5.0	-[(a)]	-	-
	DCM	490	869	502	1290	485	3.7	-[(a)]	-	-

[(a)] detected at 520 nm, there is a faster component than instrument resolution (0.4 ns), [(b)] detected at 520 nm, there is a faster component than instrument resolution (22 ps), [(c)] detected at 645 nm.

Table S2. X-ray data collection details for z*DIP3*.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	50.301	30.00	30.00	0.00	54.73	0.50	360	10.00	0.71073	50	30.0	100.00
Omega	50.301	30.00	30.00	72.00	54.73	0.50	360	10.00	0.71073	50	30.0	100.00
Omega	50.301	30.00	30.00	144.00	54.73	0.50	360	10.00	0.71073	50	30.0	100.00
Omega	50.301	30.00	30.00	216.00	54.73	0.50	360	10.00	0.71073	50	30.0	100.00
Omega	50.301	30.00	30.00	288.00	54.73	0.50	360	10.00	0.71073	50	30.0	100.00
Phi	50.301	30.00	0.00	0.00	54.73	0.50	720	10.00	0.71073	50	30.0	100.00

Table S3. Sample and crystal data for *zDIP3*.

Identification code	*zDIP3*	
Chemical formula	C44H50N4Zn	
Formula weight	700.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.220 x 0.370 mm	
Crystal habit	clear light pink prism	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 15.2910(14) Å	α = 90°
b = 15.0222(14) Å	β = 90°	β = 101.4330(10)°
c = 32.525(3) Å	γ = 90°	γ = 90°
Volume	7471.1(12) Å3	
Z	8	
Density (calculated)	1.245 g/cm3	
Absorption coefficient	0.693 mm-1	
F(000)	2976	

Table S4. Data collection and structure refinement for *zDIP3*.

Diffractometer	Bruker APEX II CCD	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	1.25 to 26.37°	
Index ranges	-19<=h<=19, -18<=k<=18, -40<=l<=40	
Reflections collected	135932	
Independent reflections	7645 [R(int) = 0.0703]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8842 and 0.7854	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7645 / 0 / 456	
Goodness-of-fit on F^2	1.065	
Δ/σ_{max}	0.001	
Final R indices	6085 data; I>2σ(I)	R1 = 0.0368, wR2 = 0.0851
	all data	R1 = 0.0546, wR2 = 0.0950
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0360P)^2+7.7287P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.362 and -0.419 eÅ^{-3}	
R.M.S. deviation from mean	0.056 eÅ^{-3}	

Table S5. X-ray data collection details for *zDIP4*.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	50.412	30.00	30.00	0.00	54.73	0.50	360	10.00	0.71073	50	30.0	99.99
Omega	50.412	30.00	30.00	72.00	54.73	0.50	360	10.00	0.71073	50	30.0	100.01
Omega	50.412	30.00	30.00	144.00	54.73	0.50	360	10.00	0.71073	50	30.0	100.01
Omega	50.412	30.00	30.00	216.00	54.73	0.50	360	10.00	0.71073	50	30.0	100.01
Omega	50.412	30.00	30.00	288.00	54.73	0.50	360	10.00	0.71073	50	30.0	100.01
Phi	50.412	30.00	0.00	0.00	54.73	0.50	720	10.00	0.71073	50	30.0	100.01

Table S6. Sample and crystal data for *zDIP4*.

Identification code	*zDIP4*	
Chemical formula	$C_{52}H_{66}N_4Zn$	
Formula weight	812.46	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.19 x 0.28 x 0.31 mm	
Crystal habit	clear orange Prism	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 14.1571(8) Å	α = 90°
	b = 12.7265(7) Å	β = 90.3010(10)°
	c = 25.3289(14) Å	γ = 90°
Volume	4563.5(4) $Å^3$	
Z	4	
Density (calculated)	1.183 Mg/cm^3	
Absorption coefficient	0.577 mm^{-1}	
F(000)	1744	

Table S7. Data collection and structure refinement for *zDIP4*.

Diffractometer	Bruker APEX II CCD	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	1.61 to 30.57°	
Index ranges	-20<=h<=20, -18<=k<=18, -36<=l<=35	
Reflections collected	107913	
Independent reflections	13814 [R(int) = 0.0458]	
Coverage of independent reflections	98.6%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8988 and 0.8411	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	13814 / 0 / 532	
Goodness-of-fit on F^2	1.024	
Δ/σ_{max}	0.002	
Final R indices	10455 data; I>2σ(I)	R1 = 0.0408, wR2 = 0.1011
	all data	R1 = 0.0631, wR2 = 0.1122
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0542P)^2+2.1872P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.528 and -0.337 eÅ^{-3}	
R.M.S. deviation from mean	0.059 eÅ^{-3}	

Table S8. X-ray data collection details for *zDIP5*.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	50.000	30.00	30.00	0.00	54.74	-0.50	360	30.00	0.71073	50	30.0	100.01
Omega	50.000	30.00	30.00	72.00	54.74	-0.50	360	30.00	0.71073	50	30.0	100.01
Omega	50.000	30.00	30.00	144.00	54.74	-0.50	360	30.00	0.71073	50	30.0	100.01
Omega	50.000	30.00	30.00	216.00	54.74	-0.50	360	30.00	0.71073	50	30.0	100.01
Omega	50.000	30.00	30.00	288.00	54.74	-0.50	360	30.00	0.71073	50	30.0	100.01
Omega	50.000	30.00	30.00	0.00	54.74	-0.50	360	30.00	0.71073	50	30.0	100.01

Table S9. Sample and crystal data for *zDIP5*.

Identification code	*zDIP5*	
Chemical formula	$C_{63}H_{82}Cl_2N_4O_4Zn_2$	
Formula weight	1160.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.290 x 0.300 x 0.390 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.958(3) Å	α = 66.687(2)°
	b = 15.459(3) Å	β = 74.418(2)°
	c = 16.517(3) Å	γ = 78.087(3)°
Volume	3132.5(11) $Å^3$	
Z	2	
Density (calculated)	1.231 g/cm^3	
Absorption coefficient	0.898 mm^{-1}	
F(000)	1228	

Table S10. Data collection and structure refinement for *zDIP5*.

Diffractometer	Bruker APEX II CCD	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	1.52 to 26.00°	
Index ranges	-17<=h<=17, -19<=k<=19, -20<=l<=20	
Reflections collected	41573	
Independent reflections	12284 [R(int) = 0.0510]	
Absorption correction	multi-scan	
Max. and min. transmission	0.7821 and 0.7209	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	12284 / 0 / 699	
Goodness-of-fit on F^2	1.133	
Δ/σ_{max}	0.249	
Final R indices	9284 data; I>2σ(I)	R1 = 0.0665, wR2 = 0.1458
	all data	R1 = 0.0933, wR2 = 0.1717
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0425P)^2+13.5881P]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0007(3)	
Largest diff. peak and hole	1.294 and -1.037 eÅ^{-3}	
R.M.S. deviation from mean	0.107 eÅ^{-3}	

Table S11. X-ray data collection details for z*DIP6*.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	50.423	30.00	30.00	0.00	54.73	0.50	360	2.00	0.71073	50	30.0	99.99
Omega	50.423	30.00	30.00	72.00	54.73	0.50	360	2.00	0.71073	50	30.0	99.99
Omega	50.423	30.00	30.00	144.00	54.73	0.50	360	2.00	0.71073	50	30.0	99.99
Omega	50.423	30.00	30.00	216.00	54.73	0.50	360	2.00	0.71073	50	30.0	99.99
Omega	50.423	30.00	30.00	288.00	54.73	0.50	360	2.00	0.71073	50	30.0	99.99
Phi	50.423	30.00	0.00	0.00	54.73	0.50	720	2.00	0.71073	50	30.0	99.99

Table S12. Sample and crystal data for *zDIP6*.

Identification code	*zDIP6*	
Chemical formula	$C_{33}H_{44}N_2O_2Zn$	
Formula weight	566.07	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.170 x 0.270 x 0.350 mm	
Crystal habit	clear orange Prism	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 13.8580(5) Å	α = 90°
	b = 17.1278(6) Å	β = 116.7540(10)°
	c = 14.5810(7) Å	γ = 90°
Volume	3090.4(2) $Å^3$	
Z	4	
Density (calculated)	1.217 Mg/cm^3	
Absorption coefficient	0.825 mm^{-1}	
F(000)	1208	

Table S13. Data collection and structure refinement for *zDIP6*.

Diffractometer	Bruker APEX II CCD
Radiation source	fine-focus tube, MoK_α
Theta range for data collection	2.03 to 31.35°
Index ranges	-19<=h<=20, -24<=k<=24, -21<=l<=21
Reflections collected	38024
Independent reflections	4848 [R(int) = 0.0443]
Coverage of independent reflections	95.5%
Absorption correction	multi-scan
Max. and min. transmission	0.8712 and 0.7601
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4848 / 0 / 182
Goodness-of-fit on F^2	1.050
Δ/σ_{max}	0.001
Final R indices	4099 data; $I>2\sigma(I)$ || R1 = 0.0318, wR2 = 0.0753
	all data || R1 = 0.0437, wR2 = 0.0801
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0379P)^2+2.2351P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.430 and -0.348 $eÅ^{-3}$
R.M.S. deviation from mean	0.063 $eÅ^{-3}$

Table S14: Fitting parameters for the PL lifetime measurements of *zDIP1-3* in different solutions

	Solvents	**a_1**	**τ_1(ns)**	**a_2**	**τ_2(ps)***
zDIP1	Cyclohexane	1	3.7 ± 0.2		
	Dichloromethane	0.227	2.2 ± 0.1	0.773	≤ 22
	Acetonitrile	0.013	1.7 ± 0.05	0.987	≤22
zDIP2	Cyclohexane	1	4.8 ± 0.3		
	Dichloromethane	0.181	2.5 ± 0.2	0.819	≤ 22
	Acetonitrile	0.089	1.4 ± 0.02	0.910	≤ 22
zDIP3	Cyclohexane	1	1.4 ± 0.2		
	Dichloromethane	0.150	2.4 ± 0.1	0.850	≤ 22
	Acetonitrile	0.067	1.4 ± 0.05	0.933	≤22

* The faster component was faster than our instrument response function (FWHM ~22 ps)

References.

1. *Observation of Triplet Exciton Formation in a Platinum Sensitized Organic Photovoltaic Device*, S. T. Roberts, C. W. Schlenker, V. Barlier, R. E. McAnally, Y. Y. Zhang, J. N. Mastron, M. E.Thompson and S. E. Bradforth, *J. Phys. Chem. Lett.*, **2011**, *2*, 48-54.