Electronic Supplementary Information for

Color-tunable Upconversion Emission from Twisted Intramolecular Charge-transfer State of Anthracene Dimers via Triplet-triplet Annihilation

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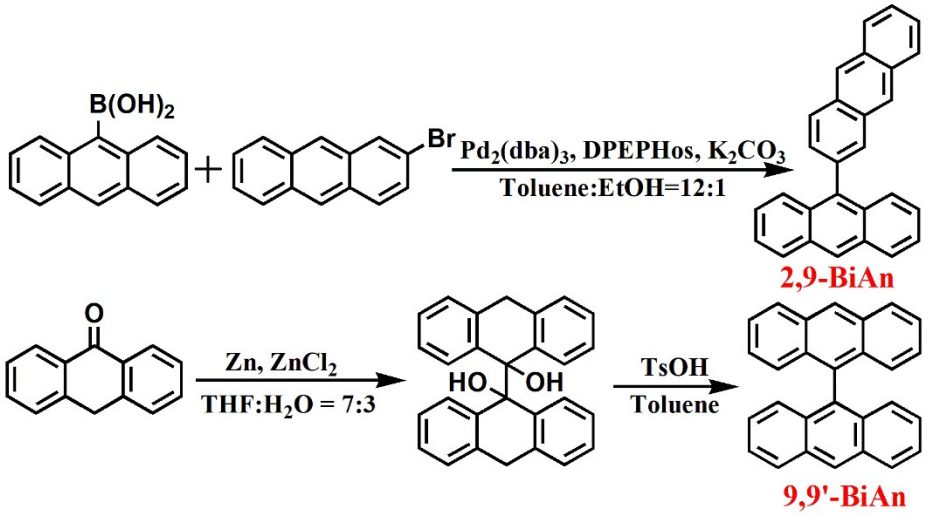
Content

1. Synthetic information

All commercially obtained reagents/solvents were used as received without further purification unless otherwise noted. 9,9'-BiAn was prepared following the literature methods and fully characterized by ^{1}H NMR and MALDI-TOF (Scheme S1).[1]



Scheme S1 The synthesis of 2,9-BiAn and 9,9'-BiAn.

2,9-BiAn:[2, 3]

9-Anthraceneboronic acid (222 mg, 1 mmol) and 2-bromoanthracene (257 mg, 1 mmol) were dissolved in a mixture of toluene (24 mL) and ethanol (2 mL) in a 50 mL flask. The flask was flushed with nitrogen. After stirring at 80 °C for 20 min, $Pd_2(dba)_3$ (12 mg, 13 μmol), DPEPHos (53.8 mg, 0.1 mmol), and aqueous 2 M K_2CO_3 (4 mL) were added to the solution. The reaction mixture was stirred at 95 °C for 10 h under nitrogen. After cooling, the resulting mixture was washed with water and extracted with chloroform for three times. The combined organic extracts were evaporated by rotavapor and purified by column chromatography on silica gel (chloroform/hexane = 1 / 9) to give the target compound (216 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.54 (s, 1H), 8.47 (s, 1H), 8.19 (d, 1H), 8.08 (d, 4H), 8.03 (d, 1H), 7.75 (d, 2H),

7.55-7.45 (m, 5H), 7.33 (t, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 136.80, 135.72, 132.12, 132.00, 131.56, 131.44, 130.98, 130.35, 130.19, 129.34, 128.43, 128.25, 128.21, 128.15, 126.85, 126.75, 126.42, 126.26, 125.60, 125.54, 125.49, 125.17. MALDI-TOF: *m/z*: calcd: 354.14 $[M]^+$; found: 353.22 $[M]^+$; Elemental analysis (%), calculated for $C_{28}H_{18}$: C 94.88, H 5.12; found: C 94.75, H 5.25.

2. Minimized molecular structures of 2,9-BiAn and 9,9'-BiAn in vacuum

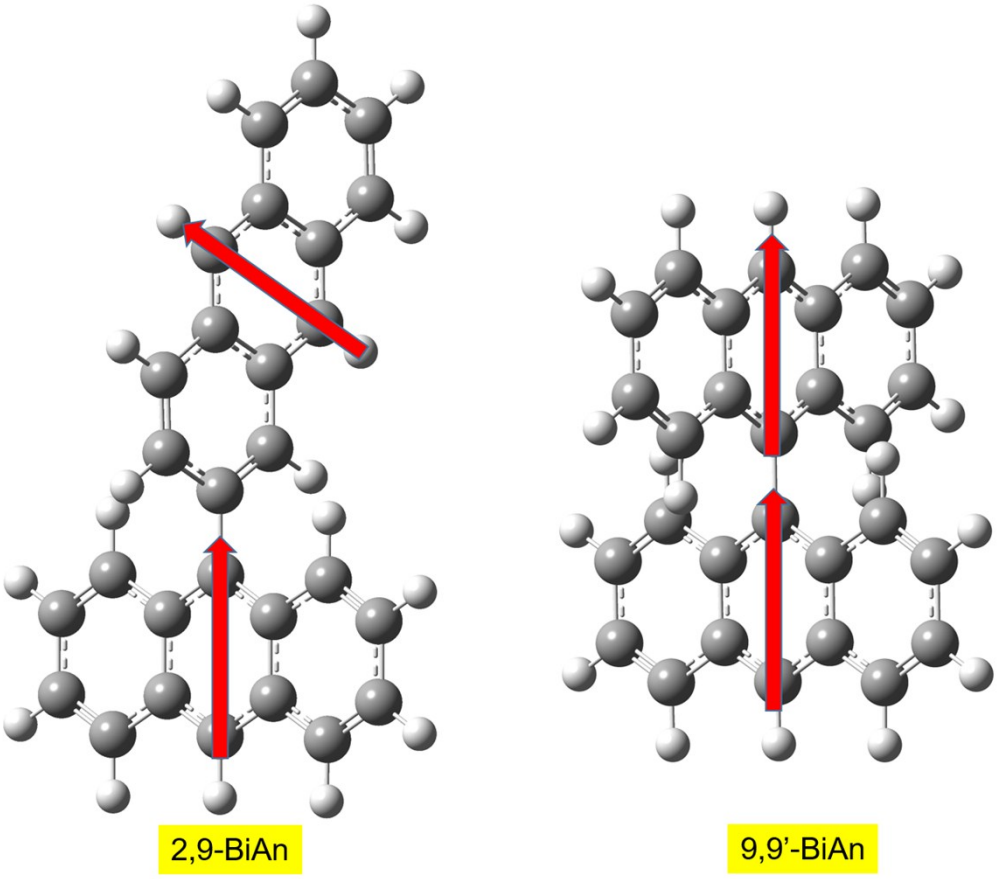


Fig. S1 Minimized molecular structure of 2,9-BiAn and 9,9'-BiAn calculated at the level of ωb97xd/6-31g (d) in the Gaussian 09 program package in vacuum.[4] The arrow represents the orientation of the transition dipole moment.

3. Solvent-dependent absorption spectra of 2,9-BiAn and 9,9'-BiAn

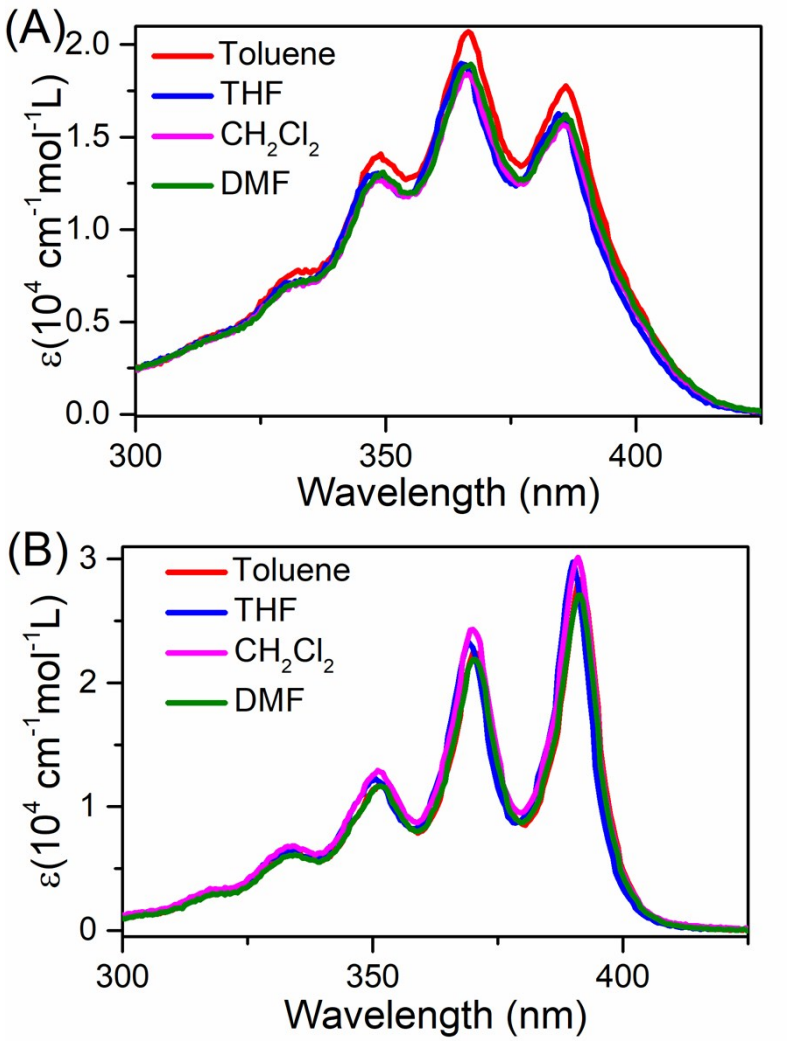


Fig. S2 Solvent-dependent absorption spectra of 2,9-BiAn (A) and 9,9'-BiAn (B).

4. Minimized molecular structure of 2,9-BiAn in toluene and DMF

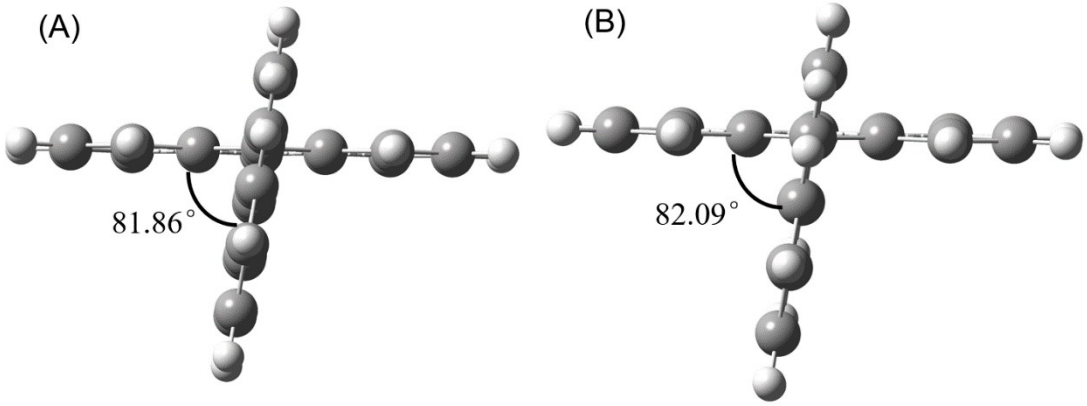


Fig. S3 Minimized molecular structures of 2,9-BiAn in the ground-state in toluene (A) and DMF (B) calculated at the level of ωb97xd/6-31g (d) in the Gaussian 09 program package. The dihedral angle between the two tetracene units is almost the same.

5. The fluorescence spectra and dynamics in different solvents

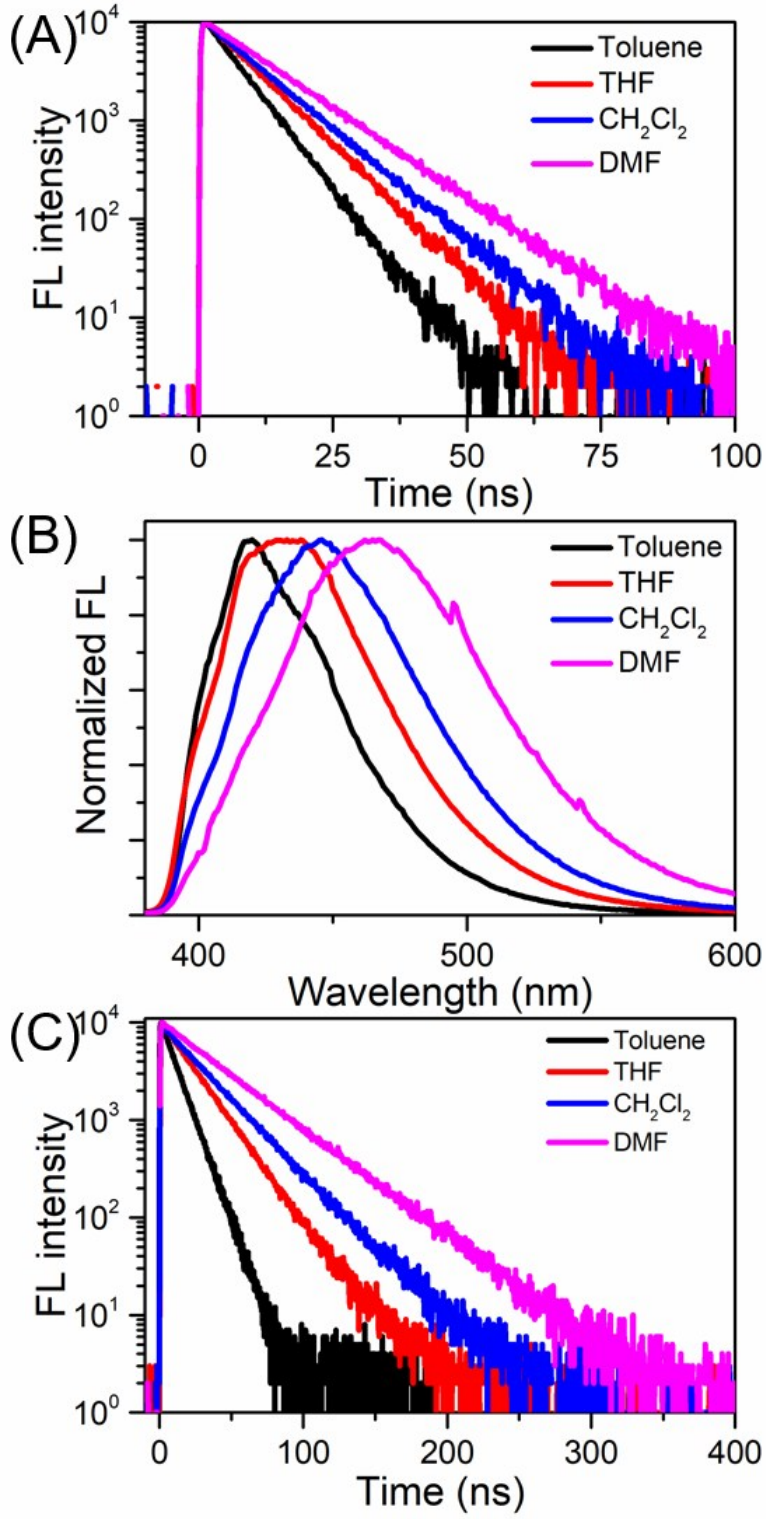


Fig. S4 Solvent-dependent fluorescence spectra (B) and dynamics (A and C) of 2,9-BiAn (A) and 9,9'-BiAn (B and C).

6. The fluorescence properties of these four compounds

Table S1 The fluorescence properties of these four compounds in different solvents.

	9-PhAn		2-PhAn		2,9-BiAn		9,9'-BiAn	
	τ/ns	Φ/%	τ/ns	Φ/%	τ/ns	Φ/%	τ/ns	Φ/%
Toluene	7.42	66.05	6.52	98%	6.07	96.42	10.40	94.14
THF					8.24	96.52	20.66	81.93
CH_2Cl_2					9.57	95.97	27.76	77.06
DMF					11.81	95.26	38.87	62.23

7. Transient absorption spectra of 9,9'-BiAn in toluene and DMF

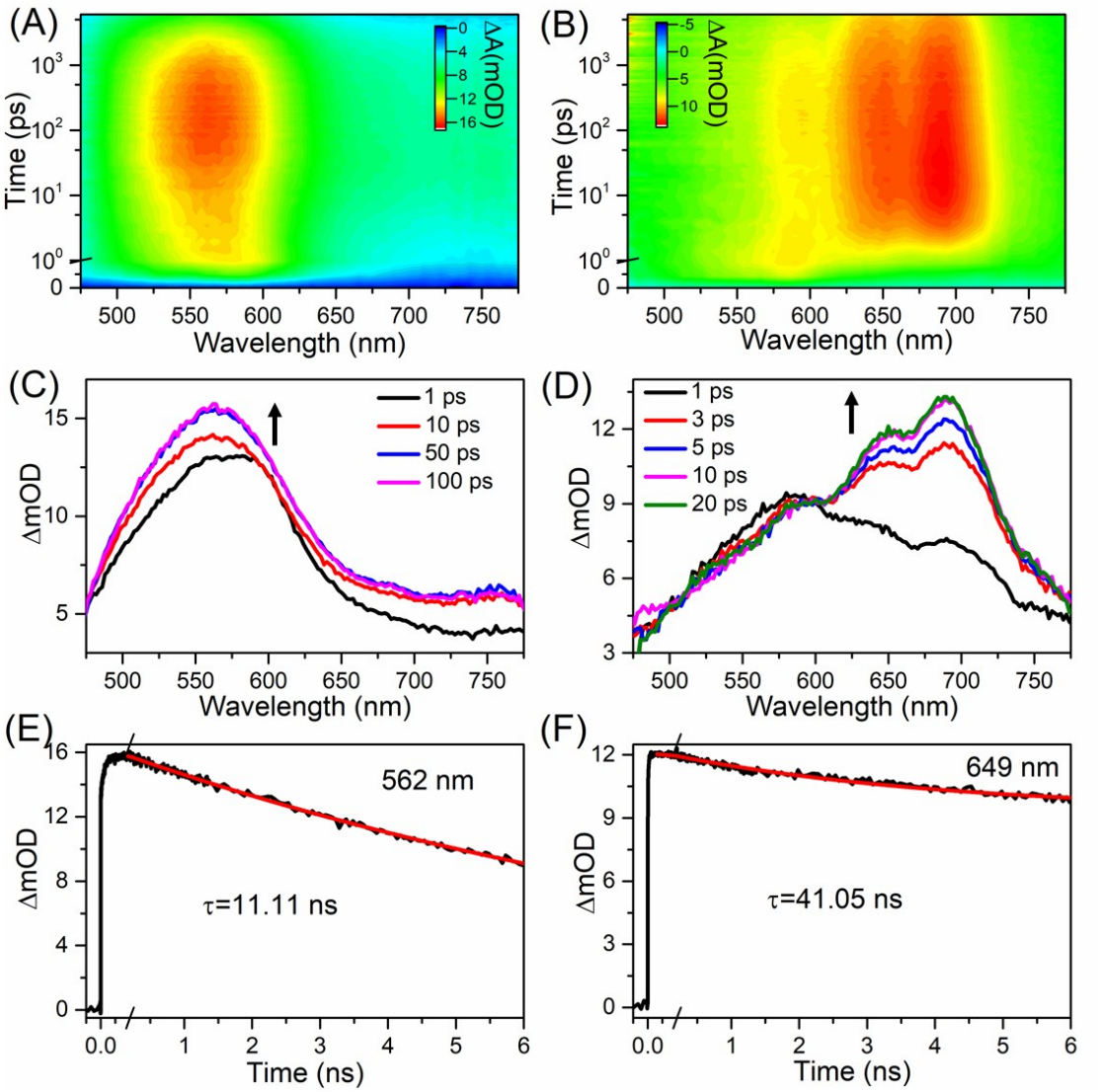


Fig. S5 (A-D) *fs*-TA spectra of 9,9'-BiAn in toluene (A, C) and DMF (B, D). (E, F) The single-wavelength dynamics of 9,9'-BiAn probed at 562 nm in toluene (E) and 649 nm in DMF (F). The red line shows the fitting result after the completion of the conversion from the LE state to the TICT state with single-exponential model.

8. Dynamics of the LE state and the TICT state of 9,9'-BiAn

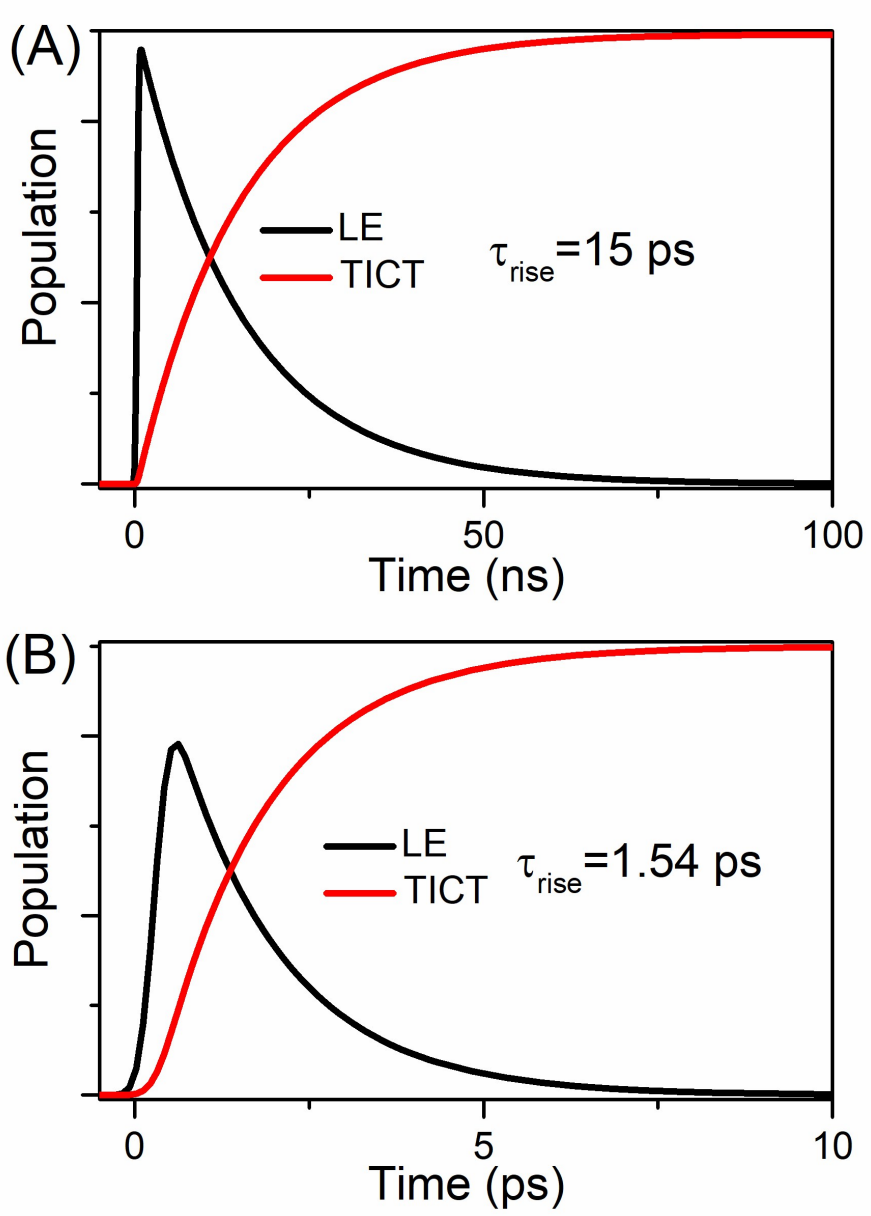


Fig. S6 Dynamics of the LE state and the TICT state of 9,9'-BiAn in toluene (A) and DMF (B).

9. The phosphorescence dynamics of the mixture of PtOEP and 2,9-BiAn or 9,9'-BiAn

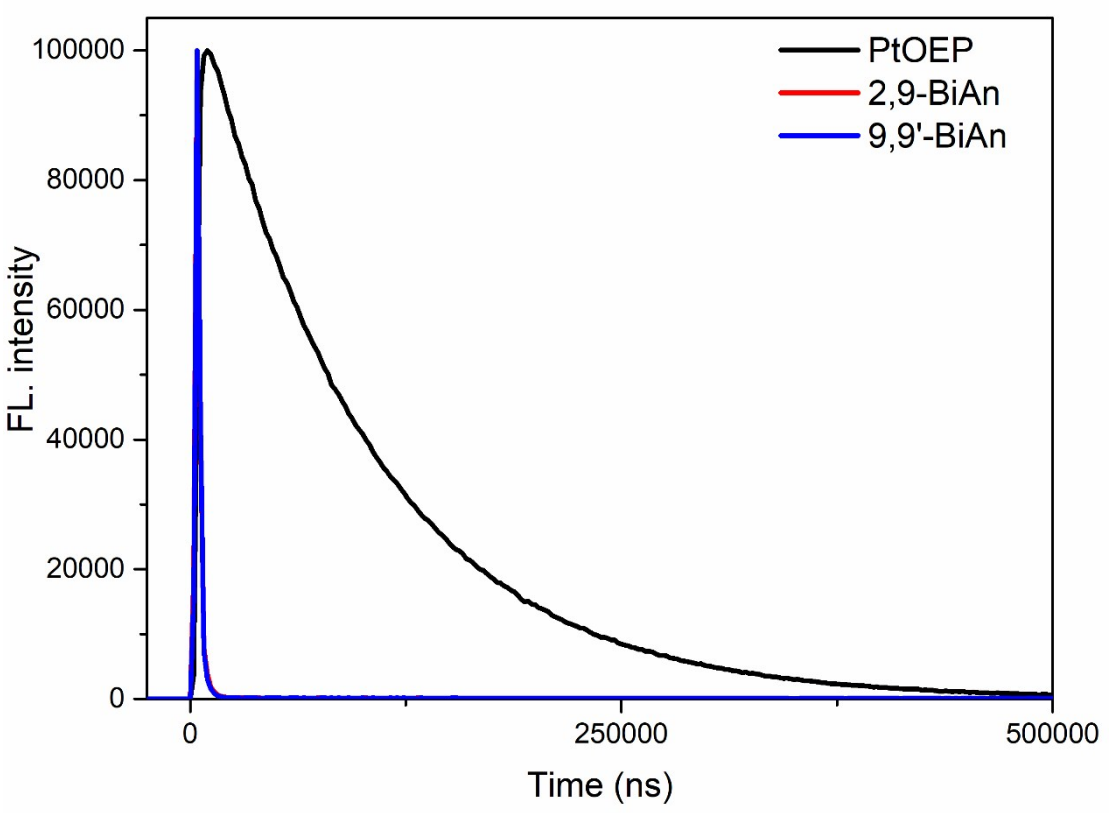


Fig. S7 The phosphorescence dynamics of the mixture of PtOEP and 2,9-BiAn or 9,9'-BiAn monitored at 647 nm with an excitation of 532 nm.

10. Comparison of the fluorescence spectra between the UC experiment and direct photoexcitation

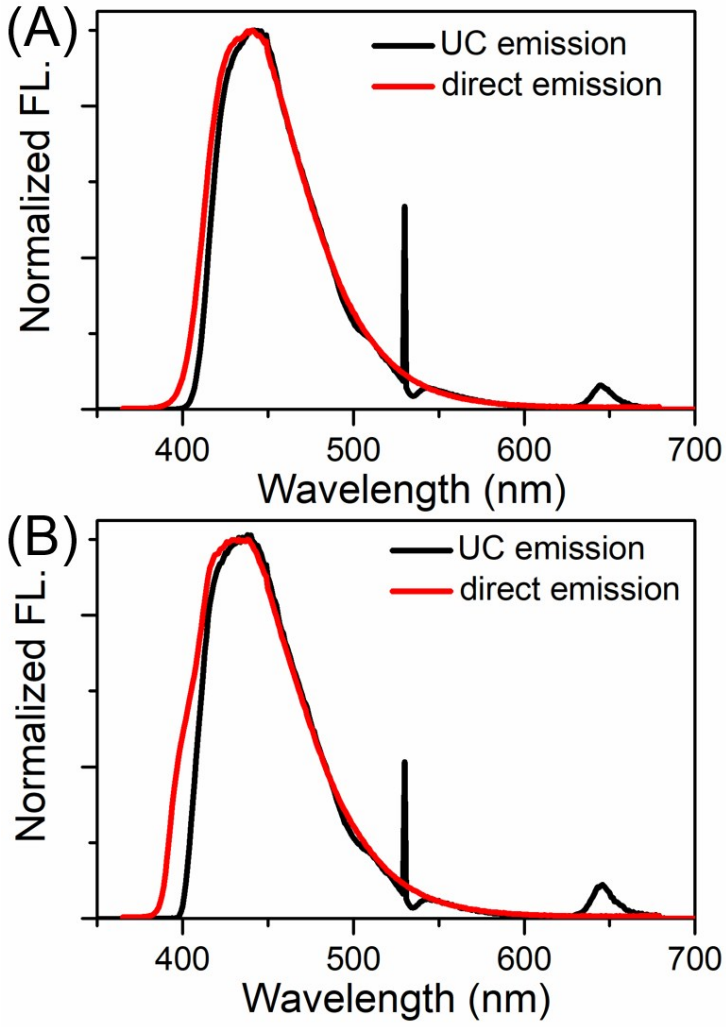


Fig. S8 Comparison of the fluorescence spectra between the UC experiment and direct photoexcitation in 2,9-BiAn (A) and 9,9'-BiAn (B) in THF.

11. Solvent-dependent Stern-Volmer plots for phosphorescence quenching of PtOEP in the mixture of PtOEP and 9,9'-BiAn

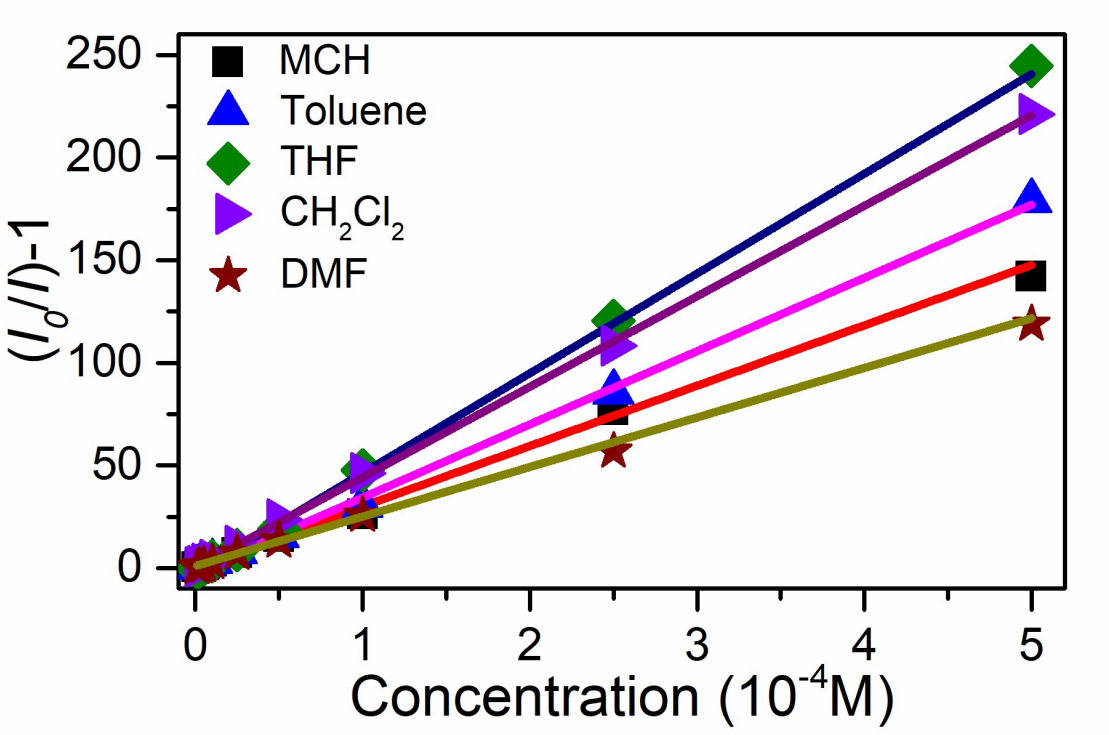


Fig. S9 Solvent-dependent Stern-Volmer plots for phosphorescence quenching of PtOEP in the mixture of PtOEP and 9,9'-BiAn. Phosphorescence was measured as a function of the concentration of 9,9'-BiAn in different solvents.

12. Dependence of fluorescence spectra on the concentration of 2,9-BiAn or 9,9'-BiAn at a constant PtOEP concentration

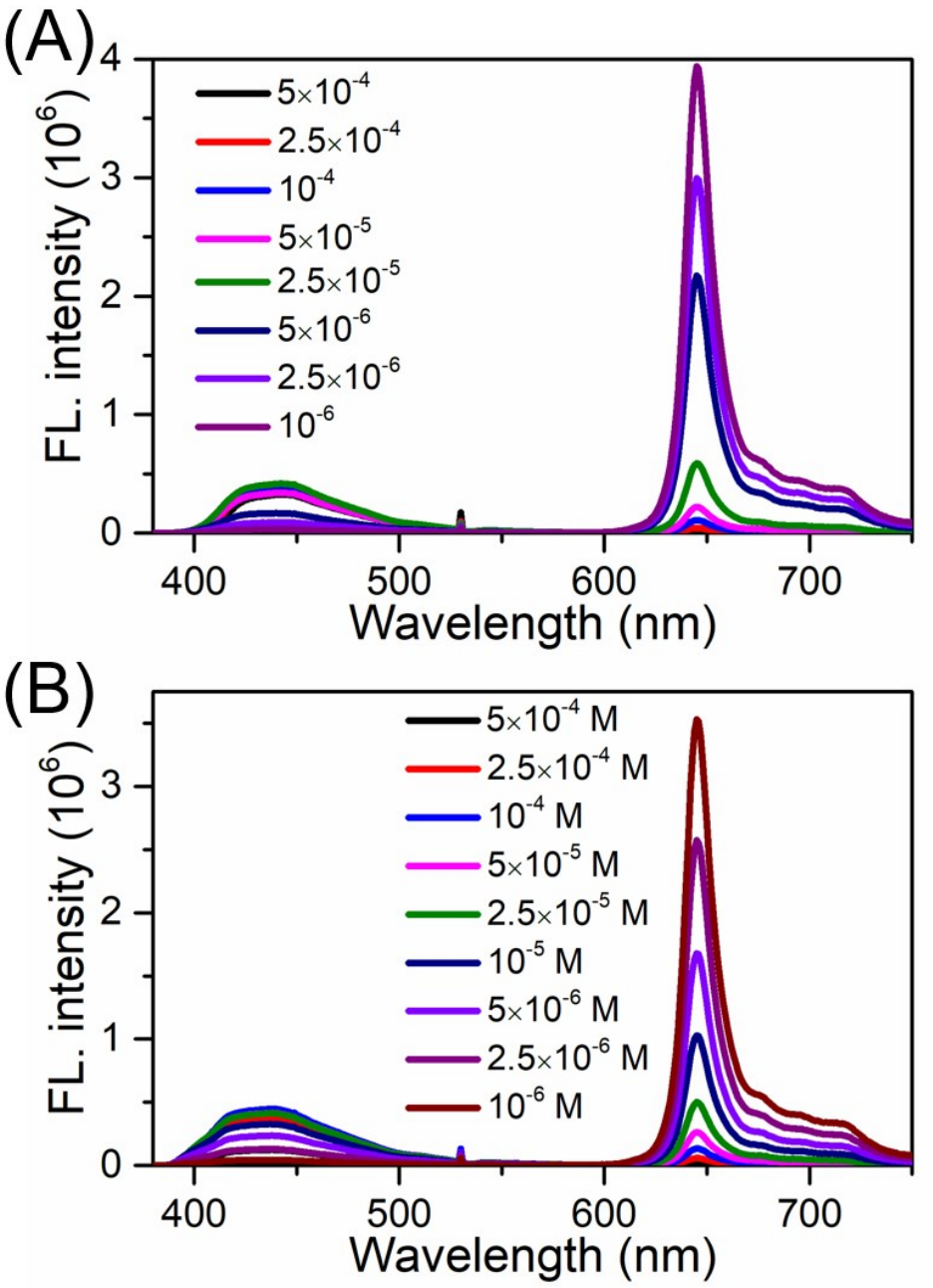


Fig. S10 Dependence of fluorescence spectra on the concentration of 2,9-BiAn (A) or 9,9'-BiAn (B) at a constant PtOEP concentration (10^{-5} M) in THF with 532 nm laser excitation (25 mw).

13. Dependence of the upconversion quantum yield on the concentration of 2,9-BiAn or 9,9'-BiAn at a constant PtOEP concentration

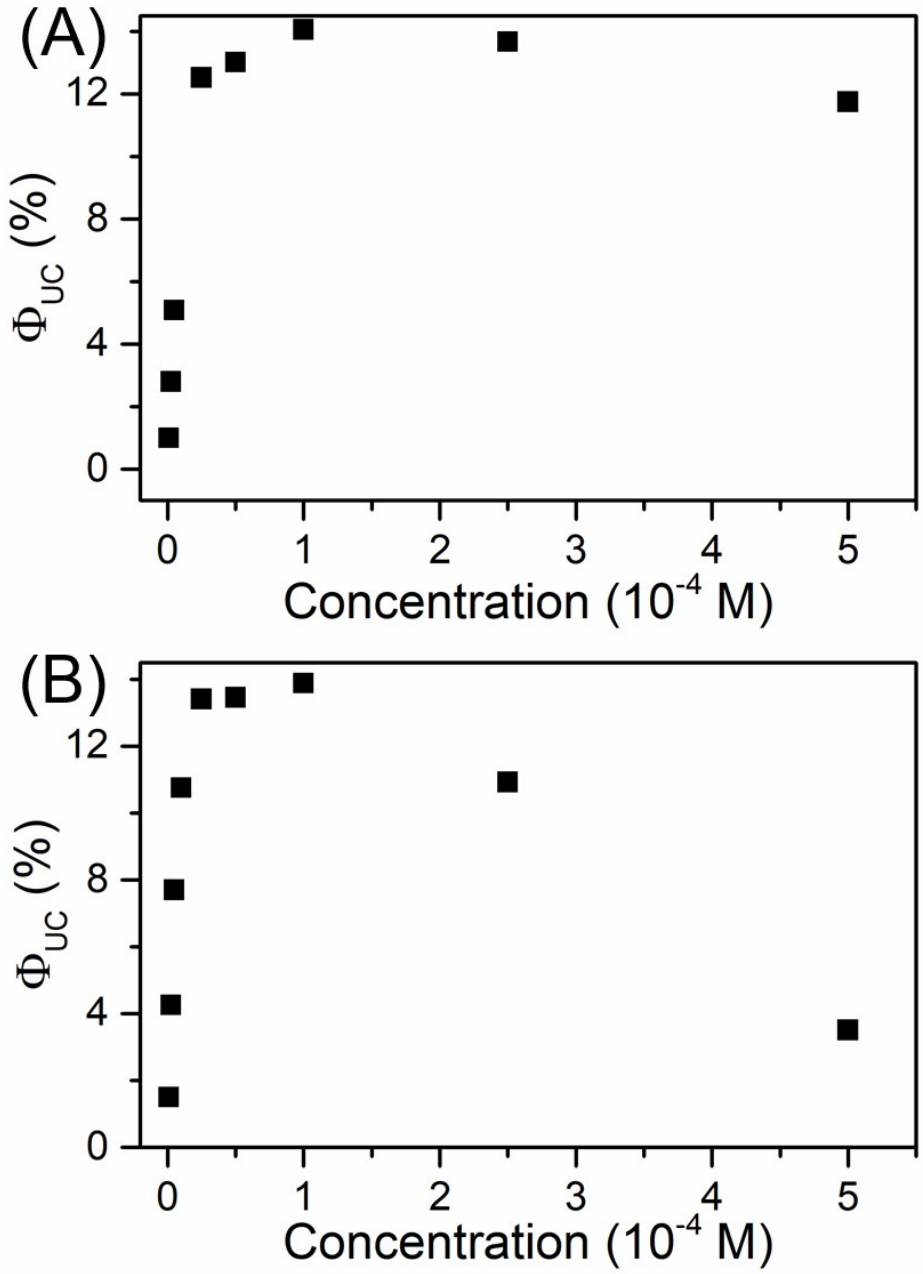


Fig. S11 Dependence of the upconversion quantum yield (Φ_{UC}) on the concentration of 2,9-BiAn (A) or 9,9'-BiAn (B) at a constant PtOEP concentration (10^{-5} M) in THF with 532 nm laser excitation (25 mw).

14. The fluorescence spectra of the mixture of PtOEP and 2,9-BiAn or 9,9'-BiAn in different solvents and the absorption spectrum of PtOEP

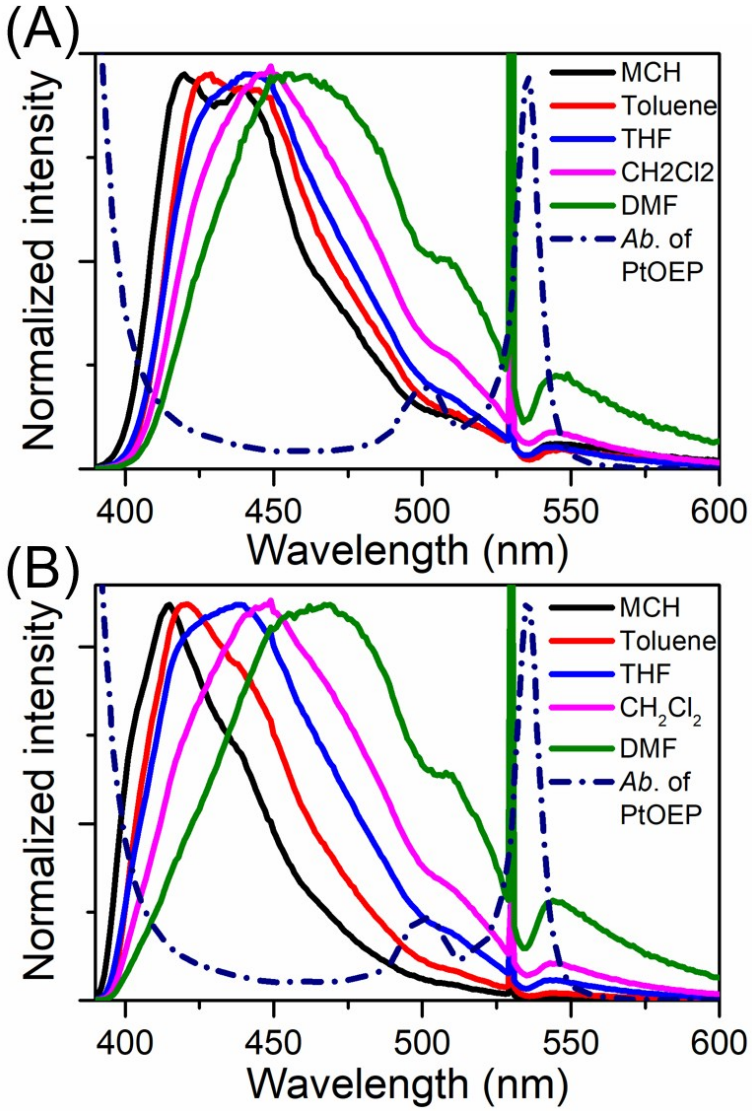


Fig. S12 The fluorescence spectra of the mixture of PtOEP (10^{-5} M) and 2,9-BiAn (A) or 9,9'-BiAn (B) (10^{-4} M) in different solvents and the absorption spectrum of PtOEP in toluene.

15. Copies of the ^{1}H NMR spectra, ^{13}C NMR spectra and MALDI-TOF spectra of 2,9-BiAn

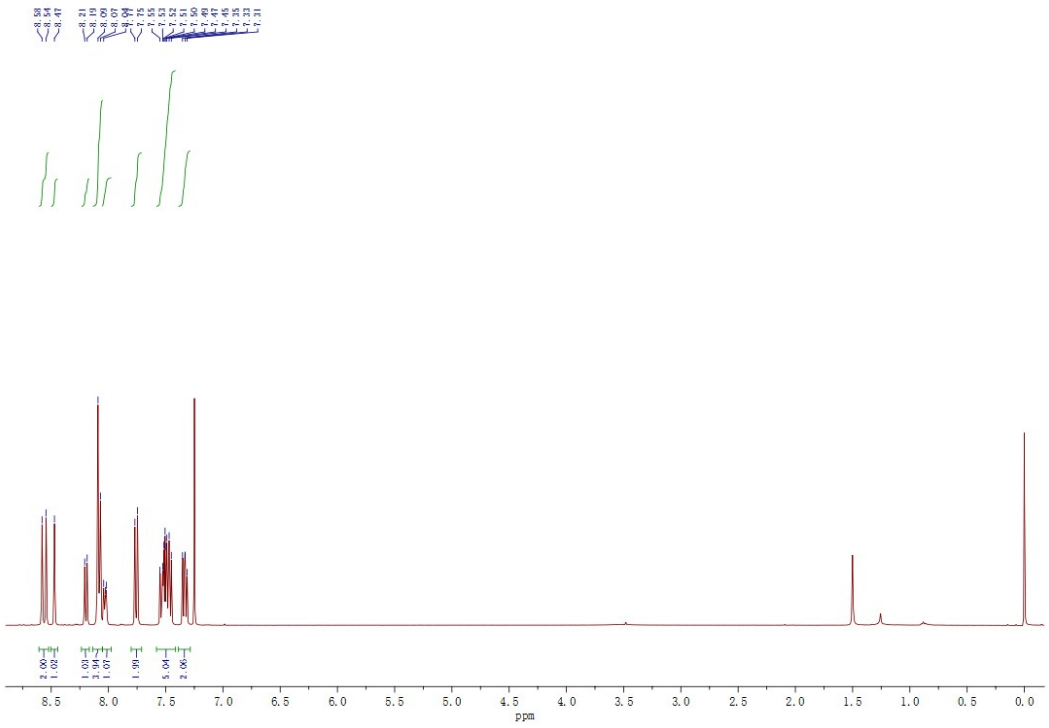


Fig. S13 The ^{1}H NMR spectrum of 2,9-BiAn.

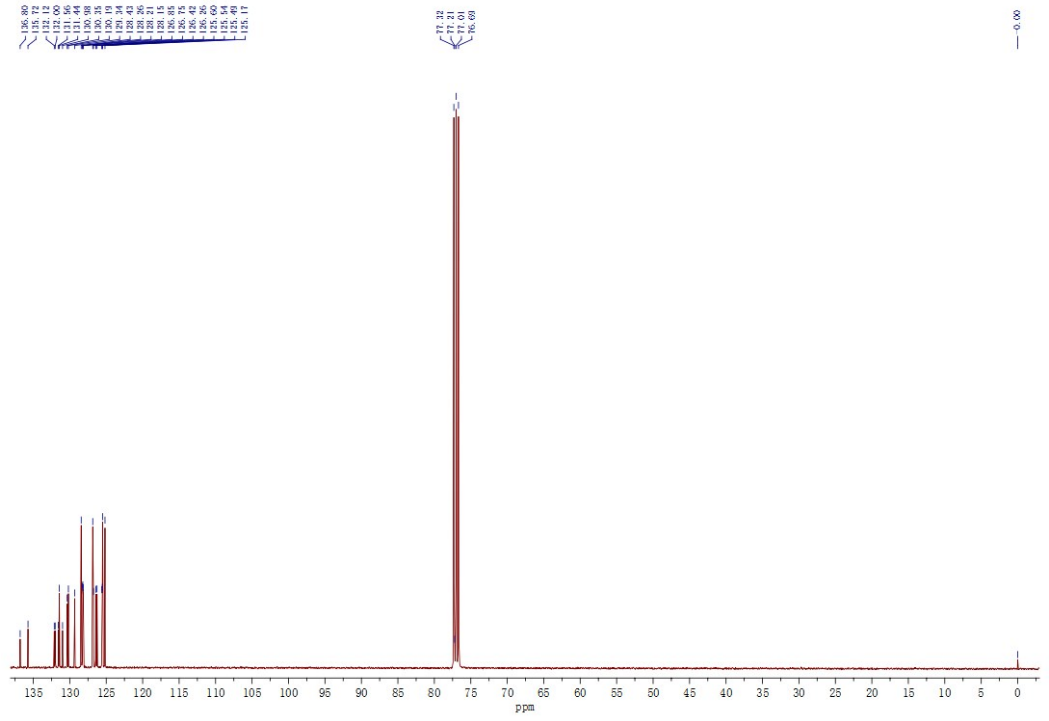


Fig. S14 The ^{13}C NMR spectrum of 2,9-BiAn.

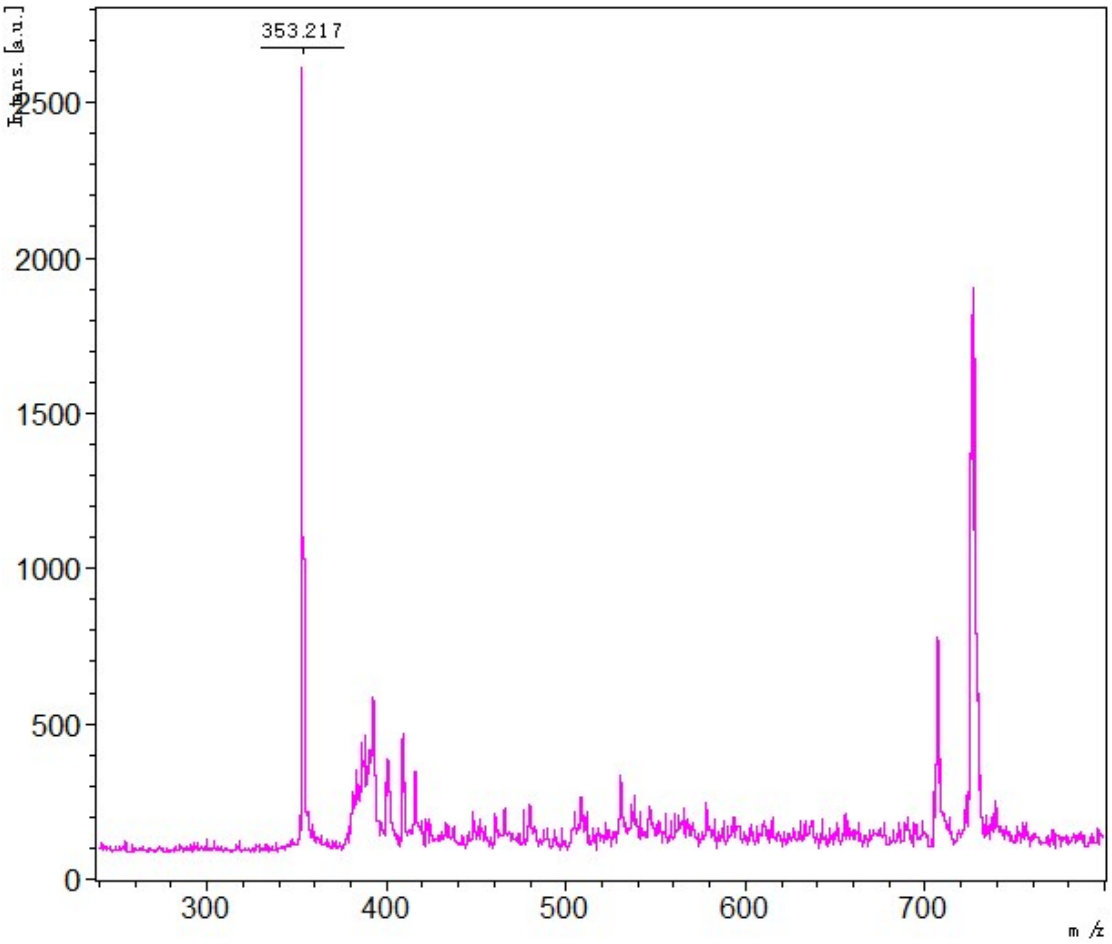


Fig. S15 The MALDI-TOF spectra spectrum of 2,9-BiAn.

Reference

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