

## Electronic Supplementary Information

### A novel thermally activated delayed fluorescence macrocycle

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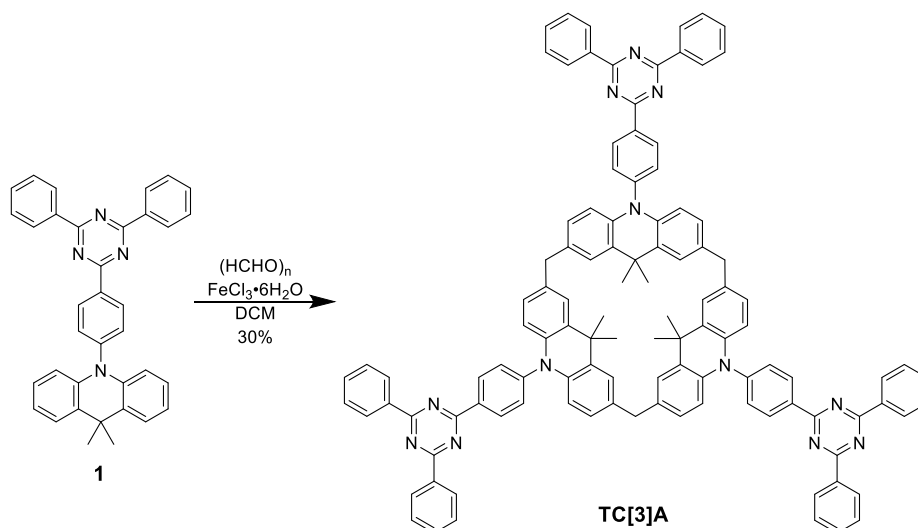
### Table of Contents

1. Materials and methods .....	S2
2. Synthetic procedures and characterized data.....	S2
3. Crystal structures and crystal data.....	S7
4. Theoretical calculations.....	S9
5. Photophysical measurements.....	S20
6. References.....	S20

## 1. Materials and methods

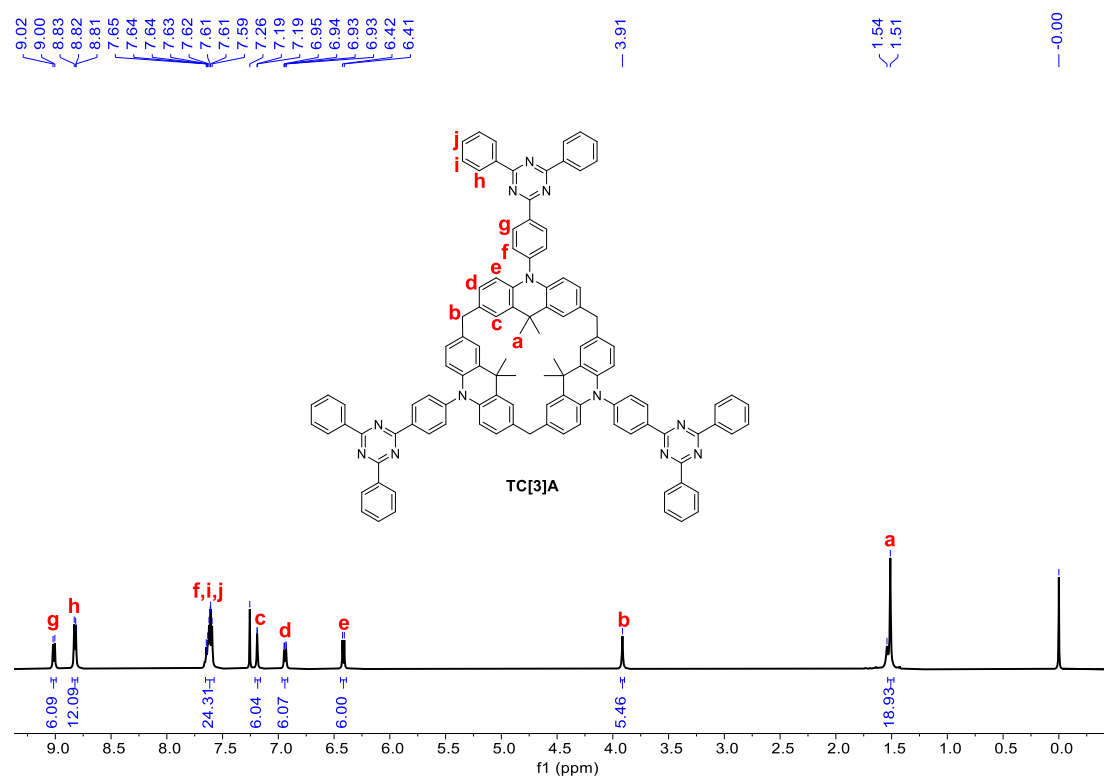
All the reagents were commercially available and used without further purification. The compound **1** was prepared according to the literature method.<sup>[S1]</sup> Anhydrous dichloromethane was dried from 4Å molecular sieves. Flash column chromatography was performed on 200-300 mesh silica gel. NMR spectroscopy experiments were recorded on the Bruker Avance III 500 MHz NMR spectrometer. High resolution mass spectra were measured on a Thermo Fisher Exactive high resolution LC-MS spectrometer. Single-crystal X-ray diffraction data were collected on a Bruker Smart APEXII CCD diffractometer using graphite monochromated Cu K $\alpha$  radiation at 170 K. UV-vis spectra were recorded on PerkinElmer Lambda 950 UV-Vis/NIR spectrometer, and photoluminescence (PL) spectra and transient PL decay characteristics were measured on an Edinburgh Instruments FLS 1000 spectrometer. Photoluminescent quantum yield (PLQY) were measured on a HORIBA FluoroMax spectrometer utilizing an integrating sphere.

## 2. Synthetic procedures and characterized data

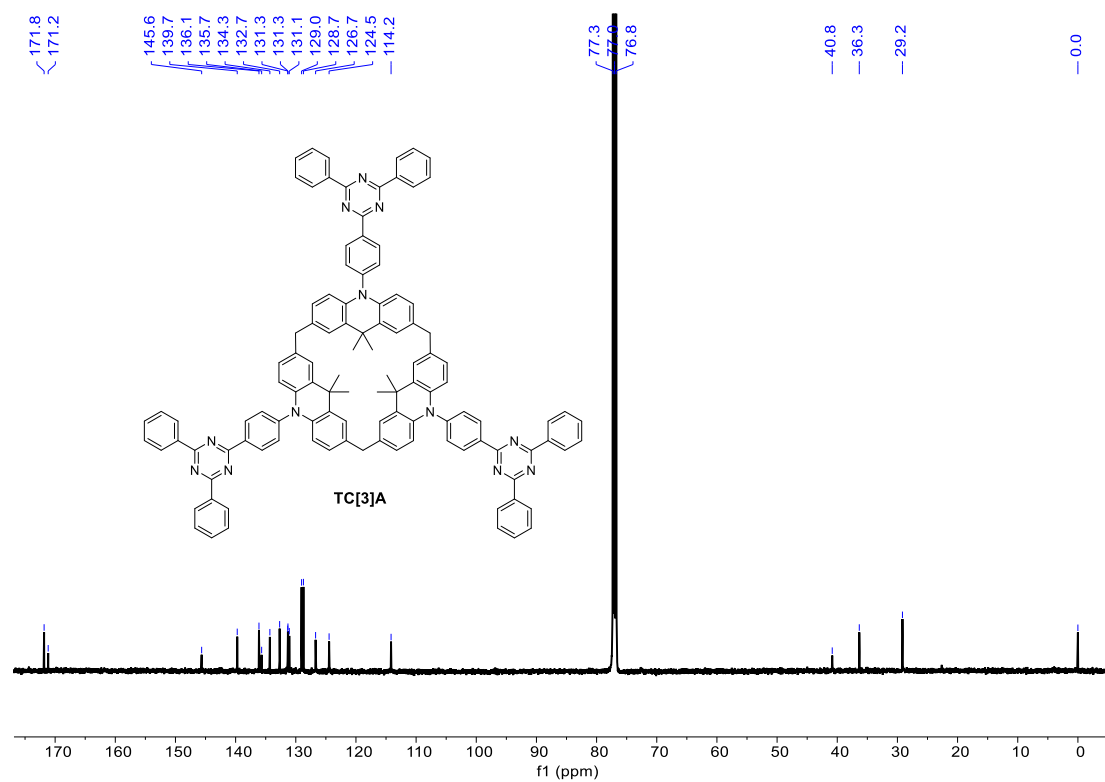


To a solution of **1** (3.00 g, 5.81 mmol) and paraformaldehyde (523 mg, 17.4 mmol) in anhydrous dichloromethane (580 mL) was added  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (2.36 g, 8.73 mmol). After continuing stirring at room temperature for 6 h, the reaction was quenched by addition of 300 mL water. Then the organic phase was separated and dried with

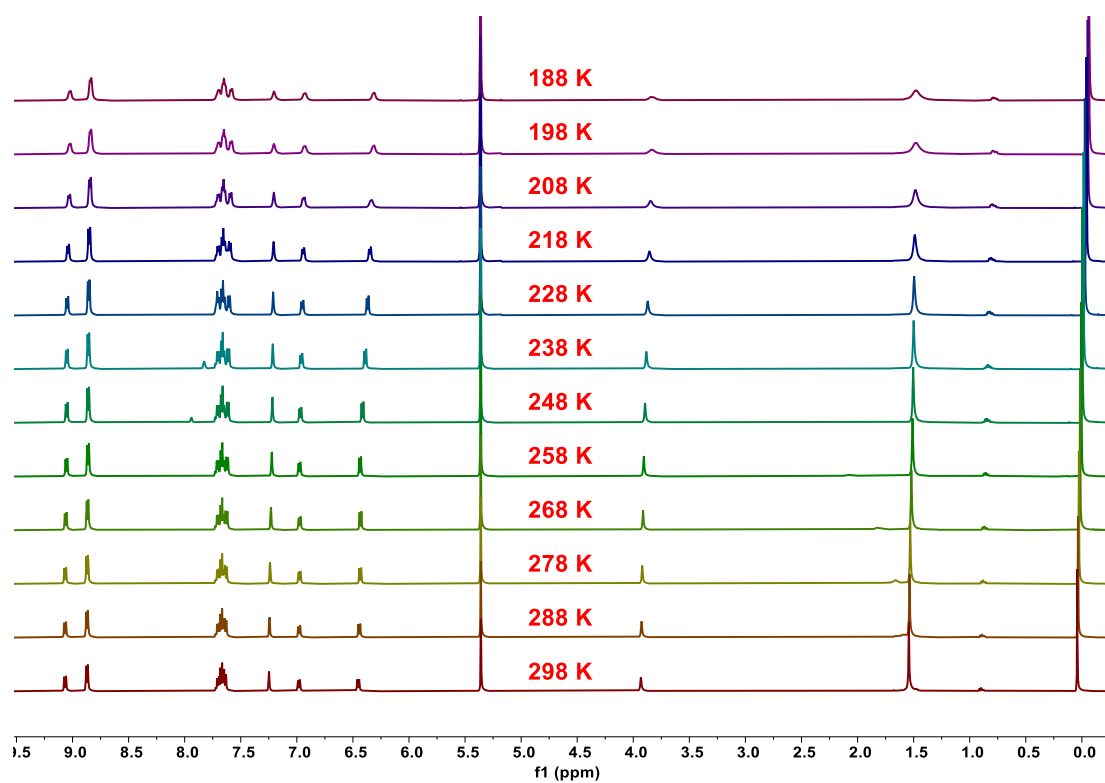
anhydrous  $\text{MgSO}_4$ . The solvent was evaporated under vacuum to give a residue, which was purified by column chromatograph ( $\text{CH}_2\text{Cl}_2$ /petroleum ether, 2:3 v/v) to yield **TC[3]A** (920 mg, 30%) as yellow solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.01$  (d,  $J = 8.1$  Hz, 6H), 8.85–8.80 (m, 12H), 7.65–7.58 (m, 24H), 7.19 (d,  $J = 2.1$  Hz, 6H), 6.94 (dd,  $J = 8.4, 1.9$  Hz, 6H), 6.42 (d,  $J = 8.2$  Hz, 6H), 3.91 (s, 5H), 1.51 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 171.8, 171.2, 145.6, 139.7, 136.1, 135.7, 134.3, 132.7, 131.3, 131.3, 131.1, 129.0, 128.7, 126.7, 124.5, 114.2, 40.8, 36.3, 29.2$ . HRMS (APCI):  $m/z$   $[\text{M} + \text{H}]^+ = 1585.7026$  (calcd. 1585.7015 for  $\text{C}_{111}\text{H}_{85}\text{N}_{12}^+$ ). Anal. calcd. (%) for  $\text{C}_{111}\text{H}_{84}\text{N}_{12}$ : C 84.06, H 5.34, N 10.60; found: C 83.65, H 5.59, N 9.96.



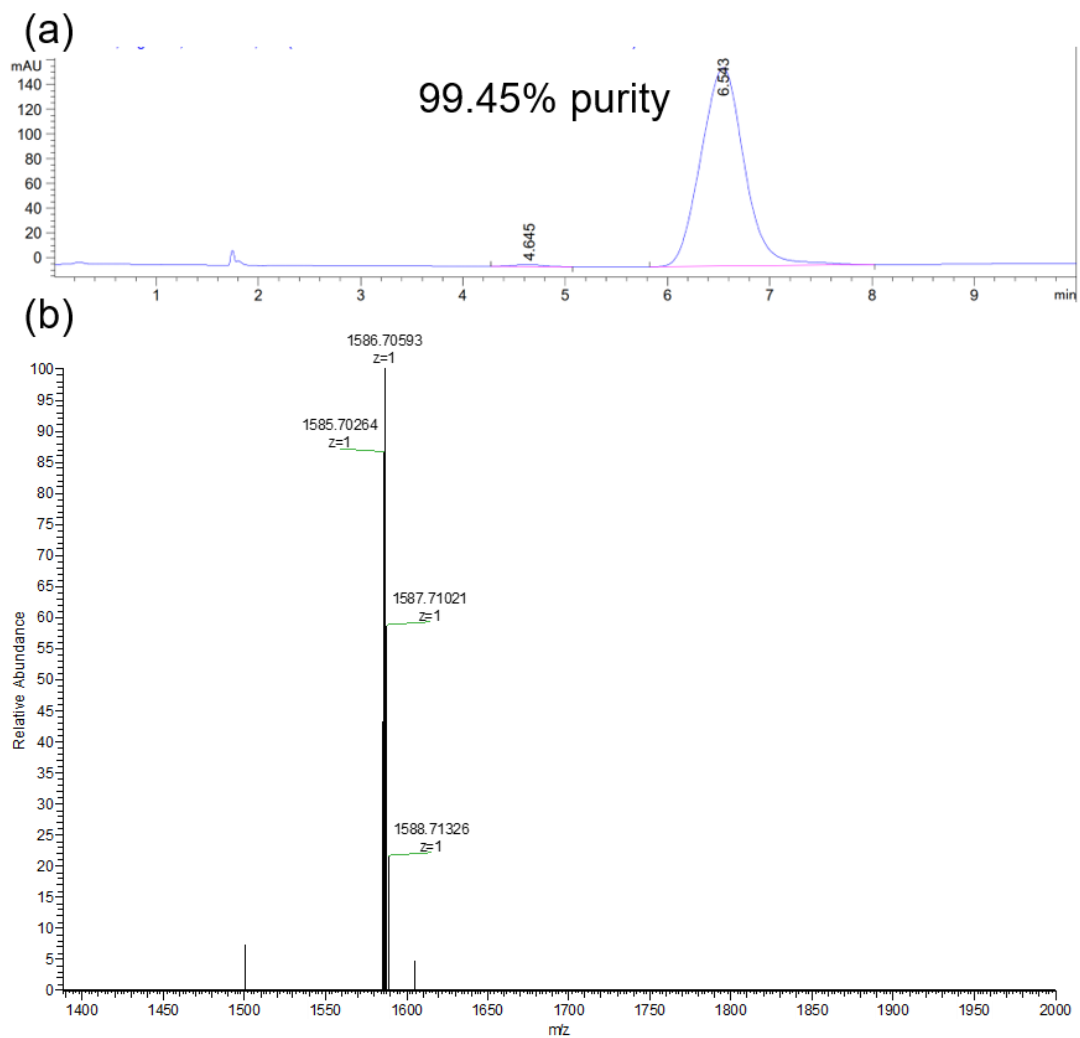
**Fig. S1**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 298 K) of **TC[3]A**.



**Fig. S2**  $^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ , 298 K) of compound TC[3]A.



**Fig. S3** Variable-temperature  $^1\text{H}$  NMR (500 MHz) spectra of TC[3]A in  $\text{CD}_2\text{Cl}_2$ .



**Fig. S4** HPLC analysis and HR-MS (APCI) spectrum of TC[3]A.

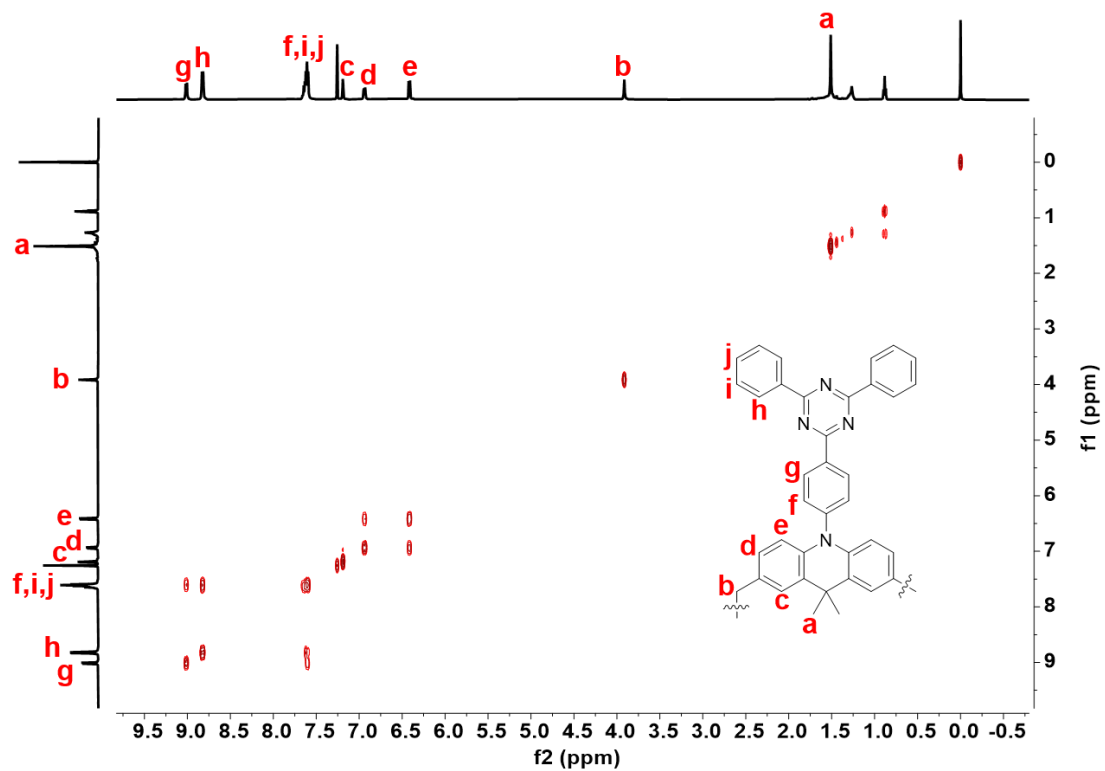


Fig. S5 2D COSY spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of TC[3]A.

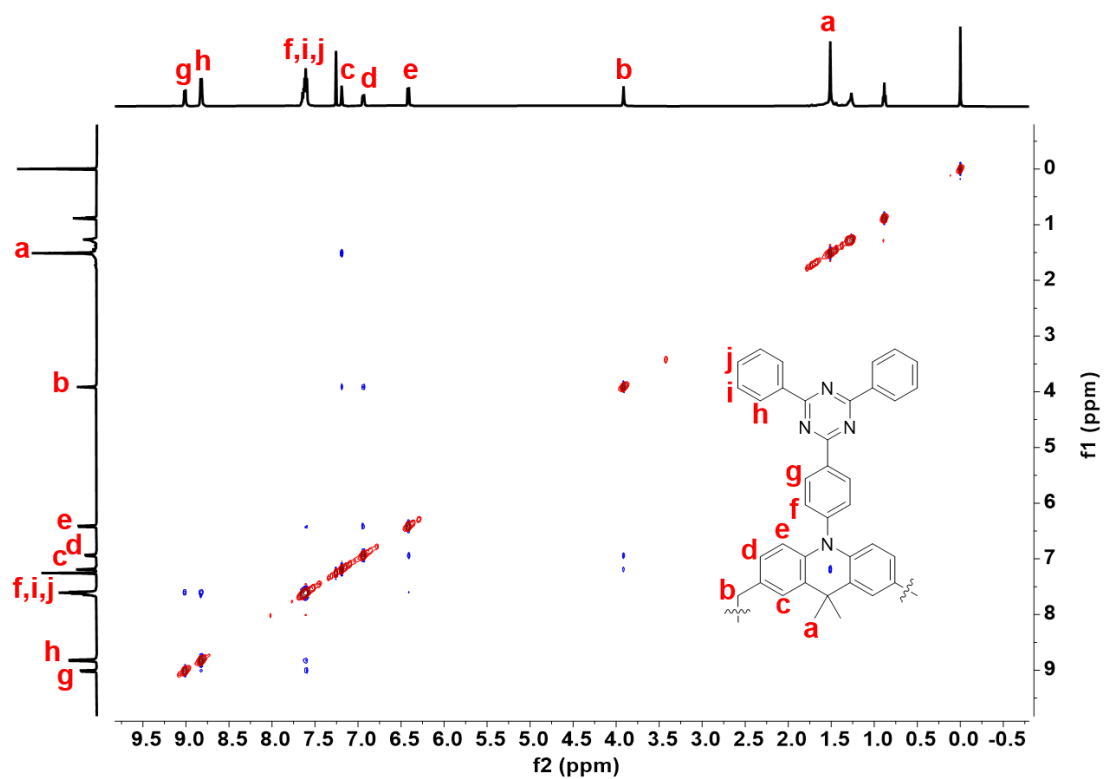
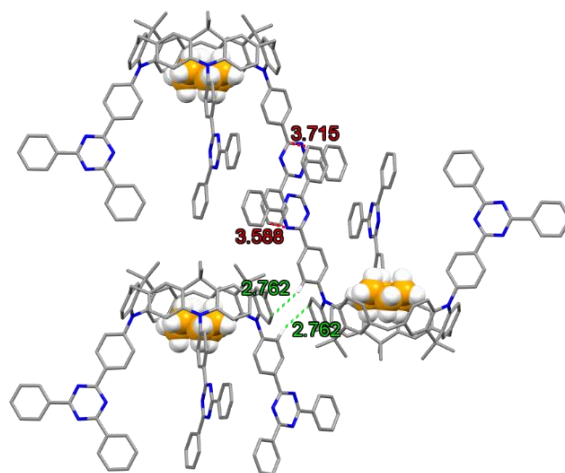
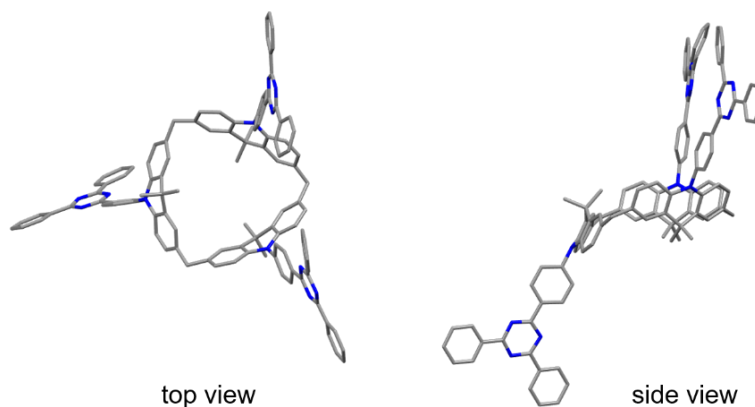


Fig. S6 2D NOESY spectrum (500 MHz, CDCl<sub>3</sub>, 298 K) of TC[3]A.

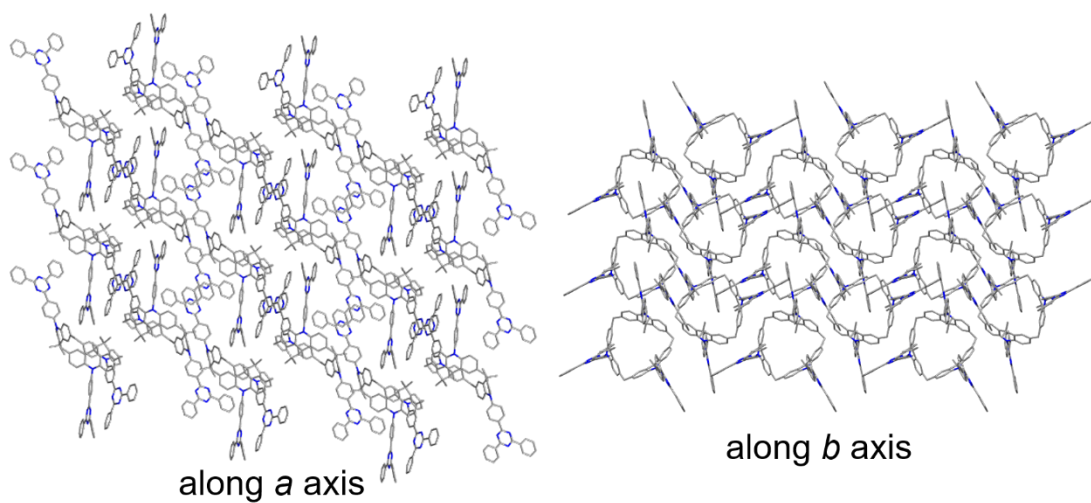
### 3. Crystal structures and crystal data



**Fig. S7** Illustration of  $\pi$ - $\pi$  stacking (red lines) and C-H $\cdots$  $\pi$  (green lines) interactions in the packing mode of TC[3]A- $\alpha$  with the cone conformation.



**Fig. S8** Crystal structure of TC[3]A- $\beta$  with the partial-cone conformation.



**Fig. S9** Packing mode of TC[3]A- $\beta$  with the partial-cone conformation.

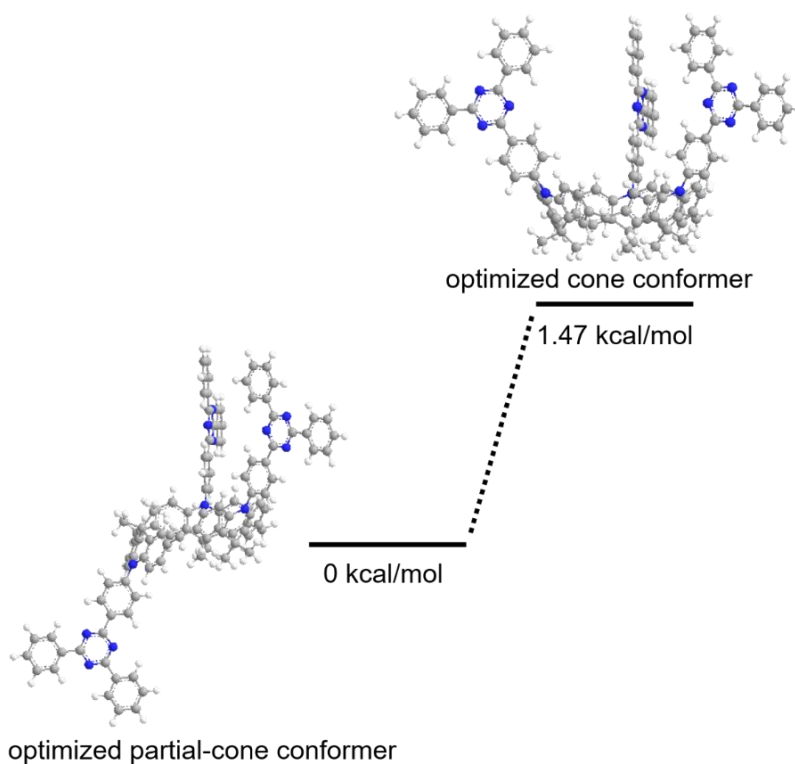
**Table S1** Crystal data and structure refinement parameters for **TC[3]A**.

Crystals	<b>TC[3]A-<math>\alpha</math></b>	<b>TC[3]A-<math>\beta</math></b>
CCDC No.	2192661	2192662
Empirical formula	C <sub>37</sub> H <sub>28</sub> N <sub>4</sub>	C <sub>111</sub> H <sub>84</sub> N <sub>12</sub>
Formula weight	528.63	1585.9
Temperature/K	169.99(13)	170.00(13)
Crystal system	trigonal	triclinic
Space group	P-3	P-1
a/Å	24.5261(4)	13.0996(2)
b/Å	24.5261(4)	18.3840(3)
c/Å	17.8430(2)	23.2467(3)
$\alpha$ /°	90	97.7680(10)
$\beta$ /°	90	90.2160(10)
$\gamma$ /°	120	109.9910(10)
Volume/Å <sup>3</sup>	9295.1(3)	5205.23(14)
Z	6	2
$\rho_{\text{calc}}/\text{cm}^3$	0.567	1.012
$\mu/\text{mm}^{-1}$	0.261	0.465
F(000)	1668	1668
Crystal size/mm <sup>3</sup>	0.520 × 0.200 × 0.005	0.300 × 0.200 × 0.100
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54184)	CuK $\alpha$ ( $\lambda$ = 1.54184)
2 $\theta$ range for data collection/°	4.952 to 150.228	3.842 to 154.746
Index ranges	-23 ≤ h ≤ 25, -29 ≤ k ≤ 30, -21 < l < 16	-16 ≤ h ≤ 15, -23 ≤ k ≤ 22, -28 ≤ l < 29
Reflections collected	37936	68701
Independent reflections	12246 [R <sub>int</sub> = 0.0341, R <sub>sigma</sub> = 0.0354]	21096 [R <sub>int</sub> = 0.0475, R <sub>sigma</sub> = 0.0392]
Data/restraints/parameters	12246/0/390	21096/0/1115
Goodness-of-fit on F <sup>2</sup>	1.342	1.092
Final R indexes [I >= 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0971, wR <sub>2</sub> = 0.3003	R <sub>1</sub> = 0.0726, wR <sub>2</sub> = 0.1647
Final R indexes [all data]	R <sub>1</sub> = 0.1075, wR <sub>2</sub> = 0.3156	R <sub>1</sub> = 0.0842, wR <sub>2</sub> = 0.1709
Largest diff. peak/hole / e Å <sup>-3</sup>	1.16/-0.40	0.38/-0.22
Crystallization solvents	cyclohexane/dichloromethane	isopropyl ether/dichloromethane

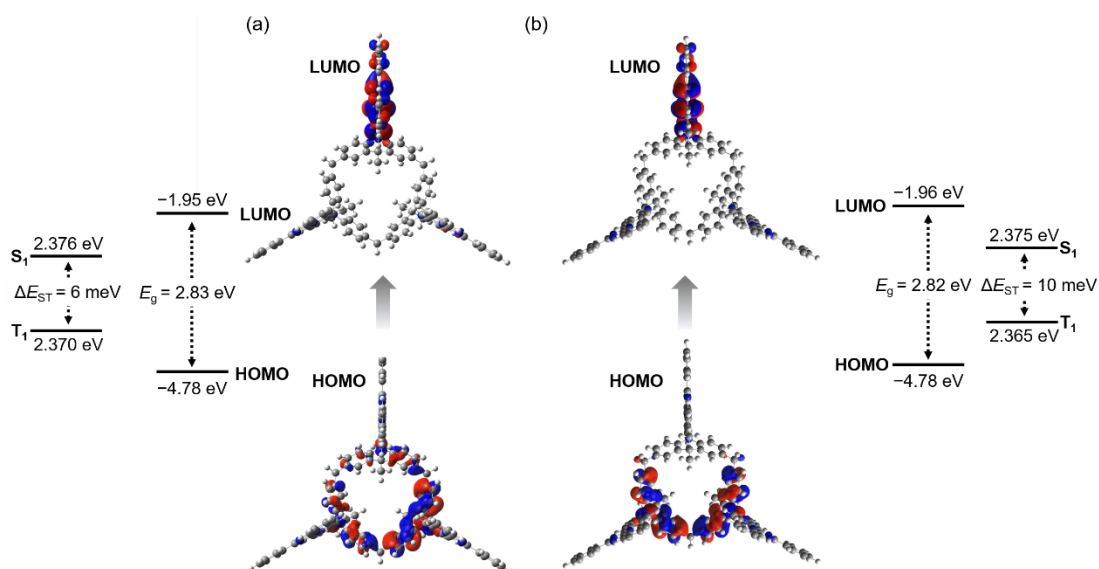


#### 4. Theoretical calculations

The conformers of TC[3]A (cone and partial-cone conformers) were optimized at the DFT level using the B3LYP exchange-correlation functional and the 6-31G(d) basis set. The calculations were performed using Gaussian 16 software package. The HOMO and LUMO were visualized with Gaussview 6.0.



**Fig. S10** Optimized structures and energy diagram of cone and partial-cone conformers of TC[3]A.



**Fig. S11** Calculated energy levels of TC[3]A: (a) cone conformer; (b) partial-cone conformer.

Cartesian coordinates of optimized TC[3]A with the cone conformation:

N	-0.95662500	5.26767700	-2.82673900
N	-1.41007000	7.77584700	3.11775200
N	-1.76633200	9.71024900	1.79212600
N	-1.79272500	9.87230600	4.15769000
C	-1.95787200	3.84032200	-4.52850300
C	-4.17128200	2.84131900	-4.15783800
C	-3.01177200	3.01327300	-4.92300300
H	-2.94272400	2.48752300	-5.86978000
C	-2.05484200	4.49806700	-3.28246900
C	-1.09656000	6.03826700	-1.62402300
C	-1.89284500	10.40872700	2.93174300
C	0.34182500	4.93169800	-3.28235800
C	-1.52579300	8.39876000	1.93572900
C	-0.75408800	4.14974400	-5.42485400
C	1.48539200	5.22463400	-2.52473700
H	1.39331400	5.75288800	-1.58330900
C	4.26654400	3.60926000	-4.60380800
H	5.04768200	4.27114800	-4.21034400
H	4.33281600	3.66418500	-5.69796100
C	-1.37761700	7.58253400	0.70510300
C	-4.26904200	3.55711300	-2.96334300
H	-5.16354500	3.47045700	-2.35047400
C	-1.34727900	7.41048600	-1.71462300
H	-1.43125900	7.86703000	-2.69606700
C	-1.55079500	8.55335300	4.20329700

C	0.48166600	4.28159300	-4.52834400
C	2.90467100	4.12098500	-4.15733000
C	-3.22837300	4.37155300	-2.52470700
H	-3.32689200	4.89804900	-1.58293100
C	-1.48685200	8.17712000	-0.56070800
H	-1.68135800	9.24131500	-0.62584200
C	-0.56391500	3.09871100	-6.53190200
H	-0.38369500	2.09954300	-6.12075300
H	0.27806500	3.36450200	-7.17785200
H	-1.44519800	3.05358800	-7.17852700
C	2.74541100	4.82620200	-2.96314100
H	3.61355500	5.05900500	-2.35045300
C	1.75851700	3.87591000	-4.92262800
H	1.87815600	3.35945600	-5.86945800
C	-1.12599600	6.20388700	0.79151800
H	-1.04200200	5.74618700	1.77038700
C	-2.16025900	11.86348300	2.82913500
C	-0.98698200	5.43858500	-0.36195800
H	-0.79262200	4.37223900	-0.29614100
C	-1.00309000	5.52609900	-6.11084600
H	-1.89996400	5.48021900	-6.73978000
H	-0.14674400	5.79788200	-6.73920000
H	-1.14683600	6.31851500	-5.37044700
C	-1.43145500	7.91404300	5.53589400
C	-1.17883200	6.53728500	5.64336500
H	-1.07305700	5.95179300	4.73732100
C	-1.56953000	8.67859800	6.70520000
H	-1.76442400	9.74112800	6.61604900
C	-1.06697200	5.93890300	6.89579800
H	-0.87134800	4.87249900	6.96839400
C	-1.45704700	8.07677500	7.95590400
H	-1.56555000	8.67716500	8.85507000
C	-1.20558800	6.70607900	8.05515200
H	-1.11802600	6.23772100	9.03200700
C	-2.27459500	12.47795300	1.57205400
H	-2.16417000	11.87153200	0.68045200
C	-2.30219100	12.64284100	3.98818100
H	-2.21288500	12.16301200	4.95600900
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H	-2.61259100	14.31068400	0.50025800
C	-2.66592400	14.61364300	2.63567700
H	-2.86200000	15.68002500	2.56064800
C	-2.55342100	14.00898400	3.89013200
H	-2.66174900	14.60365100	4.79311200

N	-4.09112900	-3.46512100	-2.81994600
N	-6.03649500	-5.10919000	3.12558200
N	-7.54525900	-6.37120800	1.80005000
N	-7.66816500	-6.48005100	4.16558000
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C	-6.52346800	-5.51457000	1.94358600
C	-3.22119100	-2.73327700	-5.41829100
C	-5.27413000	-1.32847200	-2.52066700
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C	-4.22374200	-3.57536100	-0.35513900
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C	-4.28760300	-3.63725200	-6.10564500
H	-3.79856400	-4.39220500	-6.73248100
H	-4.94930000	-3.03182700	-6.73623900
H	-4.90401500	-4.15659900	-5.36597500
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C	-5.06762200	-4.30350300	5.65079600
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C	-6.73461600	-5.70278200	6.71307500
H	-7.56267100	-6.39654900	6.62415000
C	-4.59951800	-3.91390900	6.90309300
H	-3.76843300	-3.21761900	6.97545300
C	-6.26384800	-5.31091800	7.96365700
H	-6.73035600	-5.70383400	8.86294900
C	-5.19562700	-4.41592700	8.06260600
H	-4.82921400	-4.11099000	9.03935000
C	-9.70342200	-8.17705400	1.57998600
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C	-9.82568000	-8.29131600	3.99610300
H	-9.44936300	-7.98045700	4.96391400
C	-10.76834800	-9.06936300	1.48585100
H	-11.13422000	-9.37126200	0.50825000
C	-11.36471600	-9.57501500	2.64365800
H	-12.19577600	-10.27140700	2.56866200
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N	5.04033100	-1.81295000	-2.81818000
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C	4.54658300	2.18230500	-4.15515500
C	4.11668300	1.09103700	-4.91923700
H	3.62789000	1.29283100	-5.86680800
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C	5.78036500	-2.07630100	-1.61711400
C	9.97880500	-3.56003200	2.92814400
C	4.10032000	-2.77009800	-3.27244700
C	8.05000100	-2.87837600	1.93730500
C	3.97232000	-1.43333300	-5.41738500
C	3.78093600	-3.90500500	-2.51242600
H	4.28297400	-4.08700400	-1.56972000
C	0.99458300	-5.51075300	-4.59196300
H	1.17673200	-6.51715100	-4.19569000
H	1.01069700	-5.59836400	-5.68589500

C	7.26494100	-2.60161200	0.70860500
C	5.21425100	1.91083400	-2.95968100
H	5.58575200	2.72970700	-2.34757100
C	7.09428000	-2.54436700	-1.71067400
H	7.52915400	-2.70036600	-2.69315400
C	8.20382000	-2.93024500	4.20449800
C	3.46847800	-2.56832300	-4.51930500
C	2.11803700	-4.58618700	-4.14591100
C	5.39914900	0.60303200	-2.51912400
H	5.90354400	0.42654600	-1.57662400
C	7.83130800	-2.80503800	-0.55851700
H	8.85040000	-3.16764300	-0.62602400
C	2.96705600	-1.07441400	-6.52523800
H	2.01102400	-0.73186500	-6.11473000
H	2.77774500	-1.93710400	-7.17078100
H	3.36780900	-0.28855100	-7.17225400
C	2.80637400	-4.79793500	-2.95005600
H	2.57245800	-5.66443200	-2.33547700
C	2.47956800	-3.47247900	-4.91303200
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H	5.50891900	-1.97505300	1.77789900
C	11.37312500	-4.05288400	2.82168500
C	5.20919300	-1.87133900	-0.35375100
H	4.18837800	-1.50737500	-0.28541600
C	5.28888200	-1.90679100	-6.10237400
H	5.69811400	-1.10790300	-6.73193100
H	5.09609300	-2.78491200	-6.72987700
H	6.04654500	-2.17789400	-5.36128400
C	7.59422300	-2.71363500	5.53873800
C	6.27463300	-2.24760500	5.64973900
H	5.71125100	-2.04933800	4.74519900
C	8.32983500	-2.97260500	6.70606900
H	9.34823600	-3.33221900	6.61419300
C	5.70382500	-2.04527200	6.90369100
H	4.68168500	-1.68428500	6.97901400
C	7.75573800	-2.76908300	7.95831500
H	8.33335800	-2.97244000	8.85594600
C	6.44191500	-2.30516800	8.06107000
H	5.99515700	-2.14678100	9.03912600
C	11.95821500	-4.26329600	1.56298800
H	11.37393000	-4.05983000	0.67298100
C	12.12406500	-4.31443500	3.97865800
H	11.66712800	-4.15016400	4.94774100

C	13.26801600	-4.72591700	1.46522800
H	13.71191000	-4.88567100	0.48637800
C	14.00930400	-4.98395300	2.62098600
H	15.03149400	-5.34494300	2.54314000
C	13.43359300	-4.77691600	3.87702100
H	14.00667000	-4.97634300	4.77843600

Cartesian coordinates of optimized **TC[3]A** with the partial-cone conformation:

N	5.97184200	0.00083200	-1.80701300
N	11.97287700	-0.00036400	0.60437500
N	-6.87630800	8.46410500	0.42093600
N	12.43102700	0.00003300	-1.72292800
N	-1.85255000	4.59358800	1.64788200
N	-8.78373400	8.55741700	-0.98475700
N	-1.85235500	-4.59325700	1.64709100
N	14.21665800	-0.00052100	-0.16262000
N	-7.31120300	6.70275700	-1.10701700
C	7.37579500	0.00062800	-1.50895500
C	5.25771900	-1.21951900	-1.75330800
C	5.25790800	1.22126400	-1.75269000
C	3.90586000	1.24678900	-2.16610700
C	3.78111600	-3.62253700	-1.55937800
C	3.19774700	-2.44070000	-2.03716900
H	2.15233400	-2.47258600	-2.32501900
C	3.90566700	-1.24462700	-2.16674700
C	0.53745300	-4.17810700	1.40322700
C	1.68319600	-4.23148500	0.60794300
H	2.60670400	-3.79908400	0.97713800
C	3.19812400	2.44290400	-2.03591300
H	2.15271100	2.47509700	-2.32372800
N	-6.87521800	-8.46514700	0.42078800
C	10.13150300	0.00018200	-0.96670700
C	1.70070900	-4.83121500	-0.65819500
C	-0.79287000	-2.94885200	3.09899500
C	5.86154600	-2.39783800	-1.29281300
H	6.90162700	-2.39388700	-0.98981500
N	-7.31144000	-6.70332800	-1.10624200
C	-7.98965000	9.06449000	-0.02923800
C	0.53745600	4.17914700	1.40478100
N	-8.78324400	-8.55857100	-0.98408300
C	11.58786300	-0.00006800	-0.68019300
C	8.29993400	0.00068400	-2.55775800
H	7.93614000	0.00090600	-3.58067700
C	0.51256600	-5.39707000	-1.12250300

H	0.48830700	-5.88223300	-2.09604100
C	0.54279300	-3.65571900	2.84414900
C	-1.96827000	-3.51567100	2.55863700
C	5.12944200	-3.57981000	-1.20425900
H	5.62257900	-4.47928700	-0.84189300
C	-0.79308300	2.94931700	3.09995100
C	-8.36490400	10.36927400	0.56664700
C	1.70122000	4.83282000	-0.65617800
C	3.78168200	3.62440900	-1.55753600
C	3.32056200	0.00130100	-2.84295700
C	-0.66352400	4.71629700	0.88834000
C	-9.51674000	11.04364400	0.13142900
H	-10.12445000	10.59433600	-0.64557200
C	-0.91820400	-1.82522600	3.91897100
H	-0.02213400	-1.36571600	4.32325900
C	-0.66354700	-4.71555000	0.88715500
C	9.66636000	0.00046300	-2.29008500
H	10.38682900	0.00051000	-3.09973400
C	1.68344800	4.23294100	0.60989500
H	2.60696300	3.80076800	0.97934500
C	5.86192800	2.39926200	-1.29162400
H	6.90201700	2.39499500	-0.98865300
C	7.83466300	0.00035600	-0.18482200
H	7.11323000	0.00031600	0.62684800
C	13.29884700	-0.00059900	0.81612300
C	2.98223400	-4.91184300	-1.47344600
H	2.72507600	-5.25472300	-2.48551800
H	3.63357700	-5.69307000	-1.05617000
C	0.54244500	3.65662800	2.84565700
C	-1.96846400	3.51578000	2.55918900
C	-0.65686100	-5.34080800	-0.36758300
H	-1.56845600	-5.76863800	-0.76735400
C	9.19975900	0.00013500	0.08362300
H	9.56101600	-0.00007900	1.10549900
C	5.13000900	3.58130200	-1.20246400
H	5.62329100	4.48052400	-0.83966300
C	-0.65659200	5.34170000	-0.36631400
H	-1.56817400	5.76930900	-0.76635000
C	-0.91835700	1.82555900	3.91976200
H	-0.02229500	1.36634700	4.32441300
C	0.51308500	5.39838900	-1.12083000
H	0.48902100	5.88367000	-2.09431400
C	13.73828100	-0.00018800	-1.41631700
C	-6.57827800	7.28665300	-0.14760000



C	-8.40657500	7.37527100	-1.49520000
C	-2.15566500	-1.26708200	4.26019300
C	-3.39823200	6.48618400	1.74459500
H	-2.76829900	6.91869000	2.51584400
C	-2.15575700	1.26690600	4.26037200
C	-5.35593600	6.58345100	0.31505200
C	-4.54537200	7.14622800	1.31202000
H	-4.82613400	8.10170100	1.73962900
C	-9.86774600	12.26904200	0.69202600
H	-10.76113400	12.78330500	0.34830900
C	-2.23684600	-0.00014900	5.09892600
H	-1.42500000	-0.00016200	5.83732600
H	-3.17587000	-0.00023400	5.66584600
C	-9.25198500	6.77379400	-2.55450600
C	2.98300400	4.91380900	-1.47097300
H	2.72621900	5.25742000	-2.48289000
H	3.63435700	5.69463000	-1.05295900
C	14.71385400	-0.00006800	-2.53278400
C	-7.57282000	10.94504200	1.57262200
H	-6.68460700	10.42011900	1.90496900
C	-3.04137200	5.25390900	1.18938100
C	13.77836900	-0.00096800	2.21912900
C	-3.30402700	1.89300100	3.77234500
H	-4.28630300	1.50630400	4.03473500
C	-3.21832300	2.99859300	2.93055900
H	-4.12786900	3.44914900	2.55167900
C	-3.04114000	-5.25384400	1.18887400
C	-3.21816600	-2.99902000	2.93065100
H	-4.12770600	-3.44988700	2.55212900
C	-3.30391300	-1.89357700	3.77262800
H	-4.28621900	-1.50731600	4.03555200
C	1.78165100	0.00142400	-2.83237800
H	1.37995900	0.00116700	-1.81368700
H	1.38962500	-0.87357400	-3.35852600
H	1.38976700	0.87678700	-3.35802400
C	3.79122200	0.00165200	-4.32830900
H	3.41633600	0.89276400	-4.84532700
H	3.41621300	-0.88914100	-4.84578700
H	4.88326100	0.00159500	-4.39861000
C	-5.35559500	-6.58388000	0.31501900
C	1.75015900	-2.74674500	3.13145400
H	2.68819900	-3.28764000	2.97714000
H	1.74994700	-2.42170400	4.17608900
H	1.75492000	-1.85827200	2.49108700

C	-7.92705300	12.17053500	2.13104000
H	-7.30749500	12.60787800	2.90924200
C	-6.57787400	-7.28735200	-0.14739100
C	-9.07469700	12.83594100	1.69284400
H	-9.34991900	13.79239900	2.12953300
C	12.86243800	-0.00105700	3.28305500
H	11.80148200	-0.00085000	3.06105100
C	15.15401100	-0.00123900	2.49938800
H	15.85659400	-0.00117200	1.67397800
C	-3.39740000	-6.48638700	1.74387800
H	-2.76704800	-6.91890700	2.51477800
C	0.62900500	-4.88234500	3.80068900
H	-0.20719400	-5.56966600	3.64152700
H	0.60438700	-4.55158700	4.84566600
H	1.56111000	-5.43317400	3.62828800
C	16.09305200	-0.00008900	-2.27054300
H	16.43027500	-0.00019800	-1.24039500
C	-4.99419200	-5.34570000	-0.23972100
H	-5.62174700	-4.91258400	-1.01000700
C	-3.84767700	-4.68685700	0.19266700
H	-3.56711100	-3.72953100	-0.23632400
C	-4.99392800	5.34554700	-0.23990800
H	-5.62106800	4.91244300	-1.01053900
C	-4.54448500	-7.14667700	1.31153300
H	-4.82478900	-8.10235800	1.73897900
C	-3.84736200	4.68694700	0.19271600
H	-3.56633800	3.72983200	-0.23644600
C	-8.36302800	-10.37094200	0.56634500
C	-7.98853800	-9.06575700	-0.02914200
C	-8.40674600	-7.37607400	-1.49420300
C	-10.84996700	5.63753900	-4.55755300
H	-11.46957300	5.19700700	-5.33427100
C	14.26961000	0.00007100	-3.86452800
H	13.20369200	0.00008700	-4.06131200
C	1.74999800	2.74800500	3.13329400
H	1.75524800	1.85958600	2.49285300
H	1.74954200	2.42288000	4.17790000
H	2.68791800	3.28921000	2.97934000
C	15.60271700	-0.00158900	3.81762200
H	16.66950900	-0.00180000	4.02424500
C	-10.40887700	7.43296400	-2.99945100
H	-10.67188000	8.38626000	-2.55562400
C	13.31481400	-0.00140700	4.60005100
H	12.59790800	-0.00147400	5.41661400

C	0.62794000	4.88320000	3.80234000
H	1.55993200	5.43433200	3.63031400
H	0.60305800	4.55233200	4.84727500
H	-0.20842000	5.57026600	3.64294400
C	-9.25286000	-6.77446300	-2.55287200
C	14.68531800	-0.00167400	4.87133300
H	15.03697800	-0.00194500	5.89972200
C	17.00802600	0.00003400	-3.32024500
H	18.07352000	0.00002400	-3.10702200
C	-10.40948800	-7.43406600	-2.99785800
H	-10.67176600	-8.38779900	-2.55454000
C	-7.57004000	-10.94705300	1.57141000
H	-6.68169600	-10.42209600	1.90335300
C	-8.90503000	5.53874400	-3.12467800
H	-8.01075300	5.03416800	-2.77742100
C	-11.20152900	6.86695600	-3.99466400
H	-12.09505400	7.38499000	-4.33230600
C	-9.51503700	-11.04535700	0.13165100
H	-10.12345000	-10.59578000	-0.64464600
C	-9.70010800	4.97575800	-4.11969400
H	-9.42298700	4.01938700	-4.55479400
C	-8.90684100	-5.53884900	-3.12239100
H	-8.01276200	-5.03394000	-2.77510900
C	15.18753700	0.00018400	-4.91168700
H	14.83373100	0.00028400	-5.93908000
C	-11.20279900	-6.86793100	-3.99247400
H	-12.09610300	-7.38631300	-4.33016600
C	-9.86532700	-12.27113000	0.69187400
H	-10.75885800	-12.78542100	0.34857300
C	16.55857100	0.00016800	-4.64309000
H	17.27387200	0.00026200	-5.46138100
C	-7.92355000	-12.17292900	2.12944600
H	-7.30328700	-12.61054100	2.90693400
C	-9.07137500	-12.83837200	1.69178100
H	-9.34604000	-13.79512300	2.12817900
C	-10.85217400	-5.63794800	-4.55470700
H	-11.47229800	-5.19731400	-5.33095600
C	-9.70258500	-4.97573000	-4.11679900
H	-9.42619800	-4.01891100	-4.55138300

## 5. Photophysical measurements

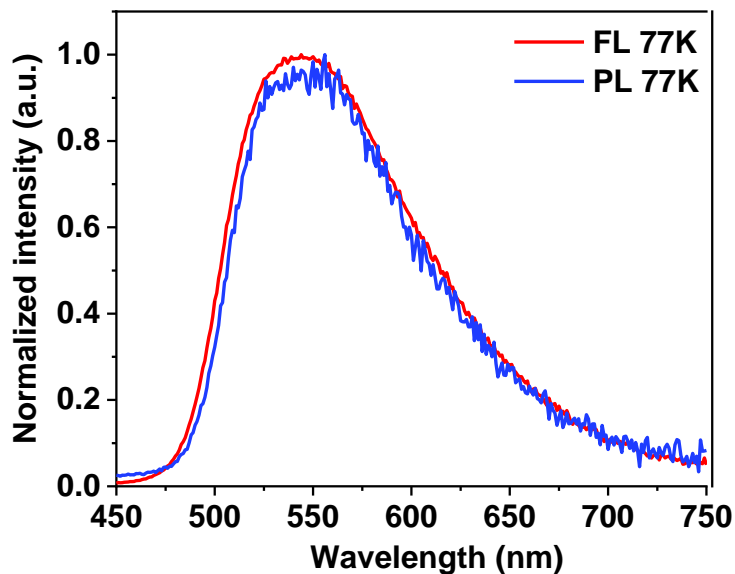


Fig. S12 Fluorescence and phosphorescence spectra of TC[3]A in neat films at 77K.

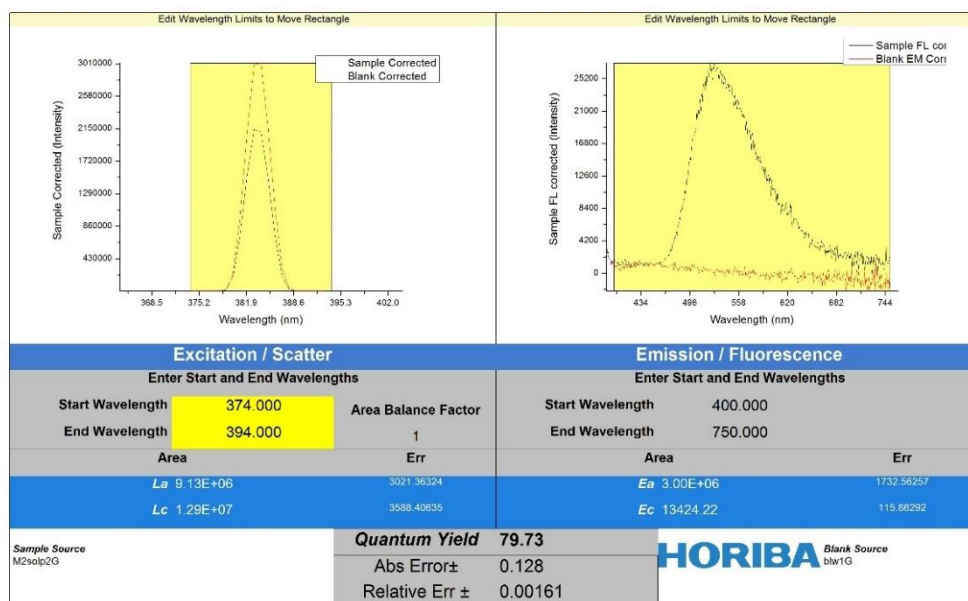


Fig. S13 PLQY of TC[3]A in diluted toluene (measured after nitrogen purging).

## 6. Reference

- S1 W. L. Tsai, M. H. Huang, W. K. Lee, Y. J. Hsu, K. C. Pan, Y. H. Huang, H. C. Ting, M. Sarma, Y. Y. Ho, H. C. Hu, C. C. Chen, M. T. Lee, K. T. Wong and C. C. Wu, *Chem. Commun.*, 2015, **51**, 13662-13665.