

Supporting Information

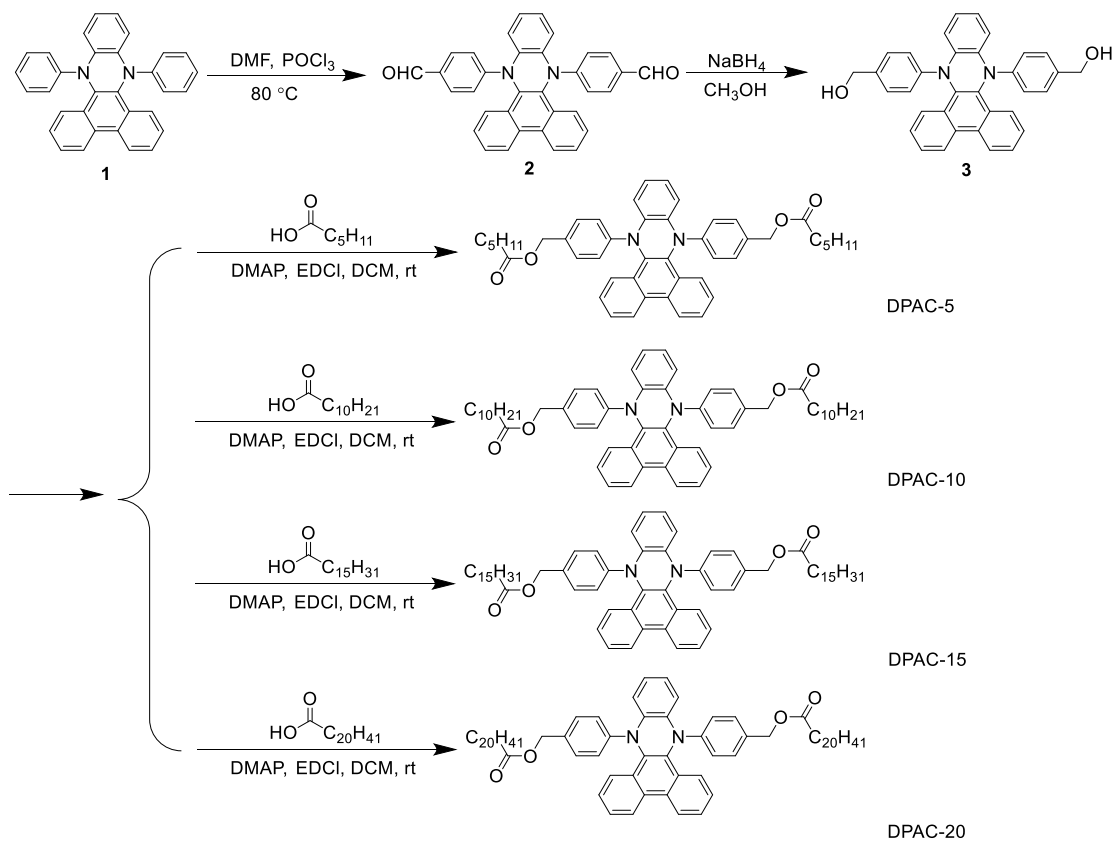
Temperature-Responsive Molecular Liquids Based on Dihydrophenazines for Dynamic Multicolor-Fluorescent Anti-Counterfeiting and Encryption

*Hao Liu,^a Wenxuan Song,^a Xuanying Chen,^a Ju Mei,^{*a} Zhiyun Zhang,^{*a} and Jianhua Su^a*

^a Key Laboratory for Advanced Materials, Feringa Nobel Prize Scientist Joint Research Center, Institute of Fine Chemicals, Joint International Research Laboratory for Precision Chemistry and Molecular Engineering, School of Chemistry and Molecular Engineering, East China University of Science & Technology, 130 Meilong Road, Shanghai, 200237, China

Table S1. Relative abilities of the currently available “similar” anticounterfeiting and encryption materials.

Sources	Materials	Abilities/Properties
This work	Temperature-responsive molecular liquids based on dual-emissive organic fluorogens	<ul style="list-style-type: none"> i) Temperature-dependent dynamic multicolor-fluorescent outputs; ii) Higher-level product security against counterfeiting; iii) Excellent reversibility and repeatability; iv) Simple preparation process; v) Solvent-free, dopant-free, and hence environment friendly; vi) Multi-modal anti-counterfeiting; vii) No requirement for complex encoding-decoding instrumentation
Ref 26	Mn ²⁺ -doped nanoparticles	<ul style="list-style-type: none"> i) Multilevel anti-counterfeiting with high-throughput rate; ii) Binary temporal codes generation for efficient data encoding; iii) Without the need for complex time-gated decoding instrumentation
Ref S1	Photoswitchable fluorescent liquid crystal polymeric nanoparticles	<ul style="list-style-type: none"> i) Aggregation-induced emission enhancement feature; ii) Water-dispersible; iii) High contrast; iv) Good repeatability
Ref 34	Graphene quantum dots	<ul style="list-style-type: none"> i) Environment friendliness; ii) Low cost; iii) Easy preparation; iv) Order-sensitive stimulus-responsive information encryption
Ref S2	Lanthanide-doped nanoparticles	<ul style="list-style-type: none"> i) Readily deposited or patterned as films to create multicolor barcodes; ii) Flexibility in high-density data storage; iii) Multidimensional information memory



Scheme S1. Synthetic route to DPAC-5, DPAC-10, DPAC-15, and DPAC-20.

The original spectra

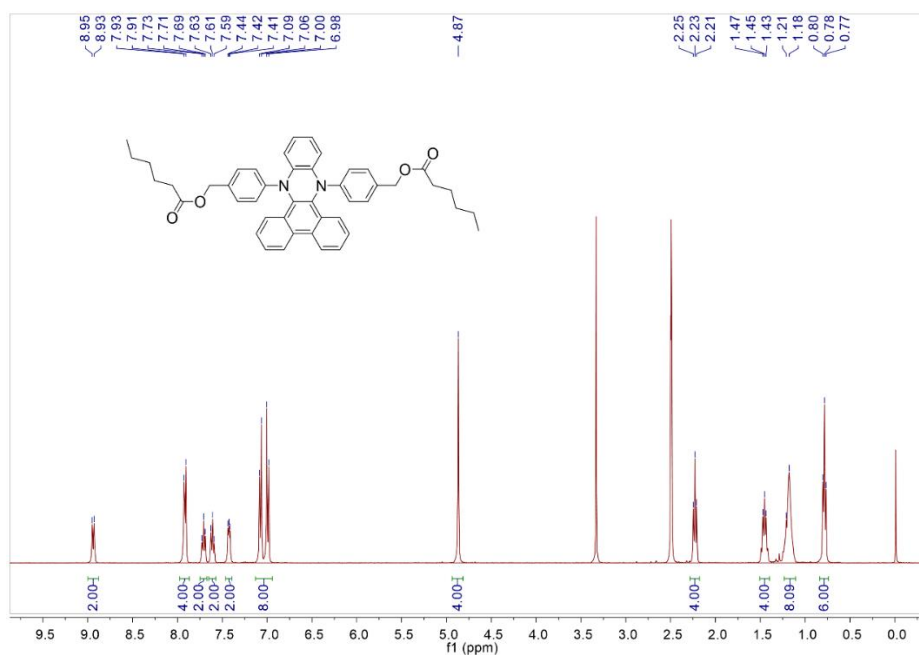


Figure S1. ^1H NMR spectrum of DPAC-5 in $\text{DMSO-}d_6$.

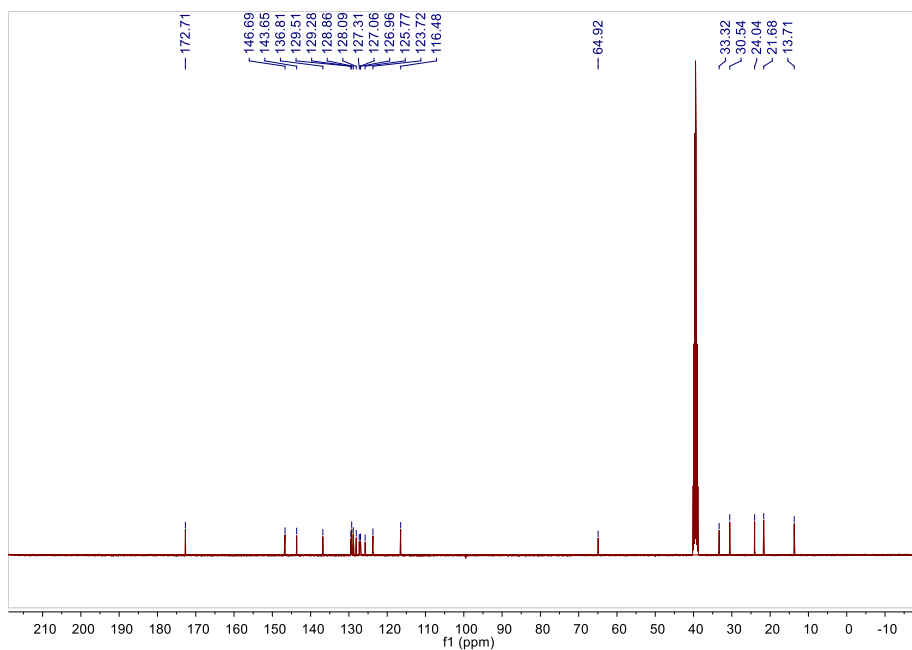


Figure S2. ^{13}C NMR spectrum of DPAC-5 in $\text{DMSO-}d_6$.

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

16 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

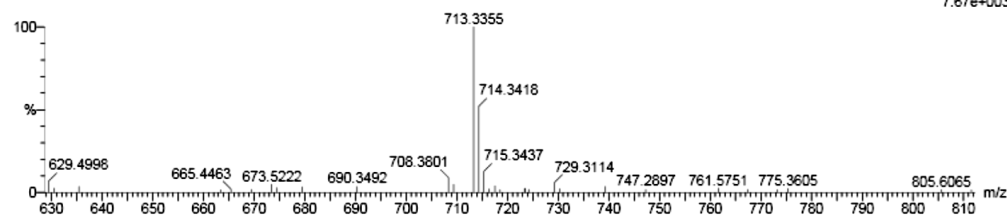
Elements Used:

C: 0-46 H: 0-46 N: 0-2 O: 0-4 Na: 0-1

H-TIAN

TH-LH-08 70 (0.794) Cm (68:70)

1: TOF MS ES+
7.67e+003



Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
713.3355	713.3355	0.0	0.0	24.5	13.9	0.0	C46 H46 N2 O4 Na

Figure S3. HRMS spectrum of DPAC-5.

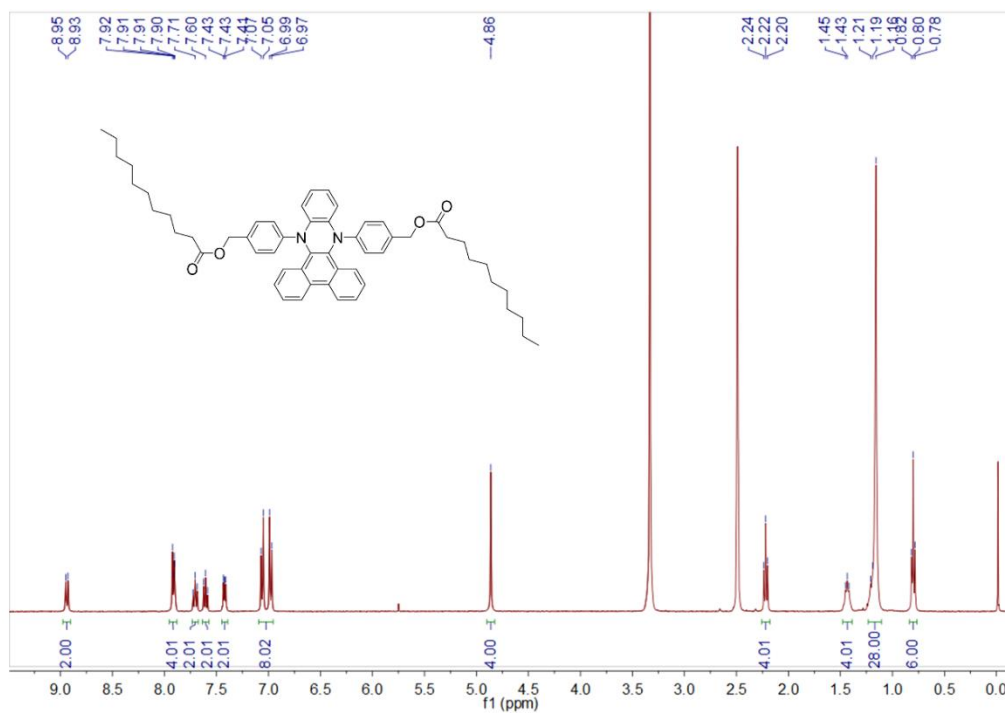


Figure S4. ^1H NMR spectrum of DPAC-10 in $\text{DMSO-}d_6$.

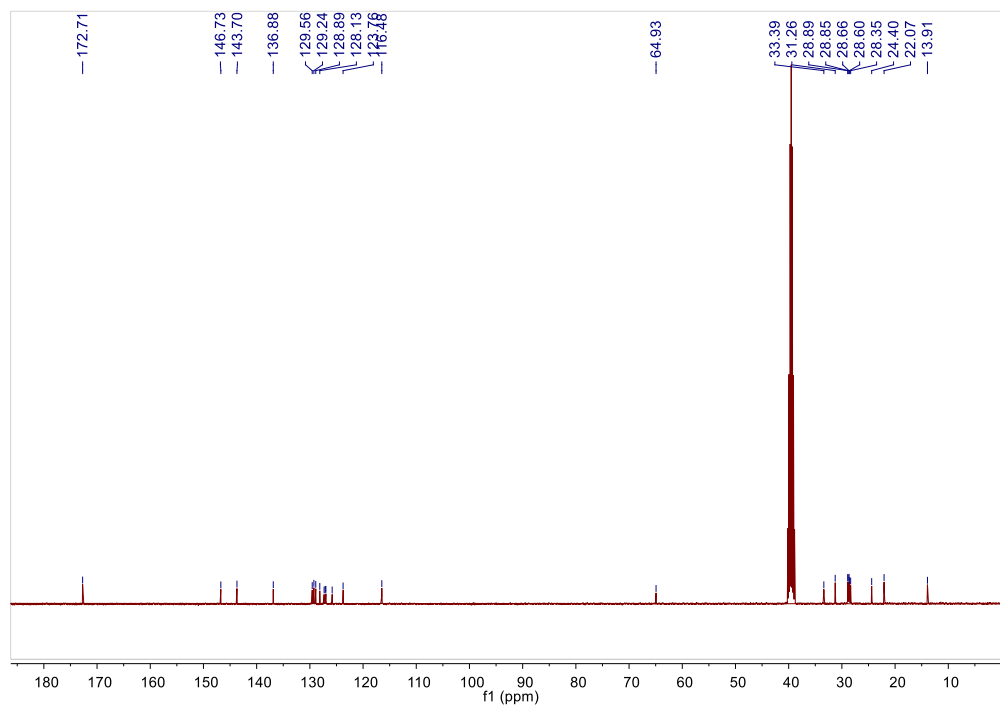


Figure S5. ^{13}C NMR spectrum of DPAC-10 in $\text{DMSO-}d_6$.

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

16 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-56 H: 0-66 N: 0-2 O: 0-4 Na: 0-1

H-TIAN

TH-LH-09 34 (0.379) Cm (32:34)

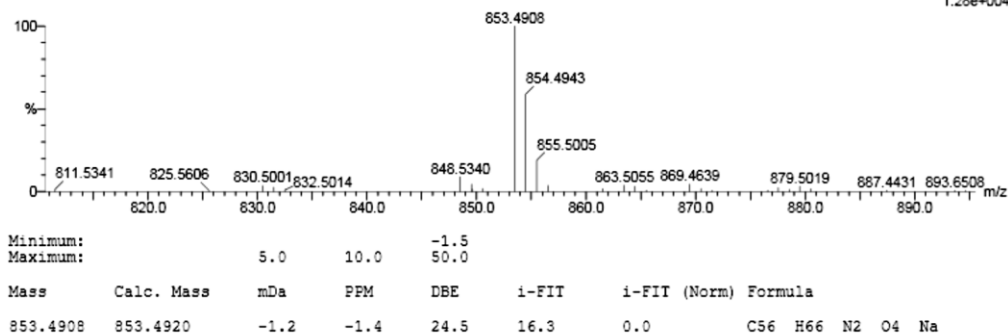
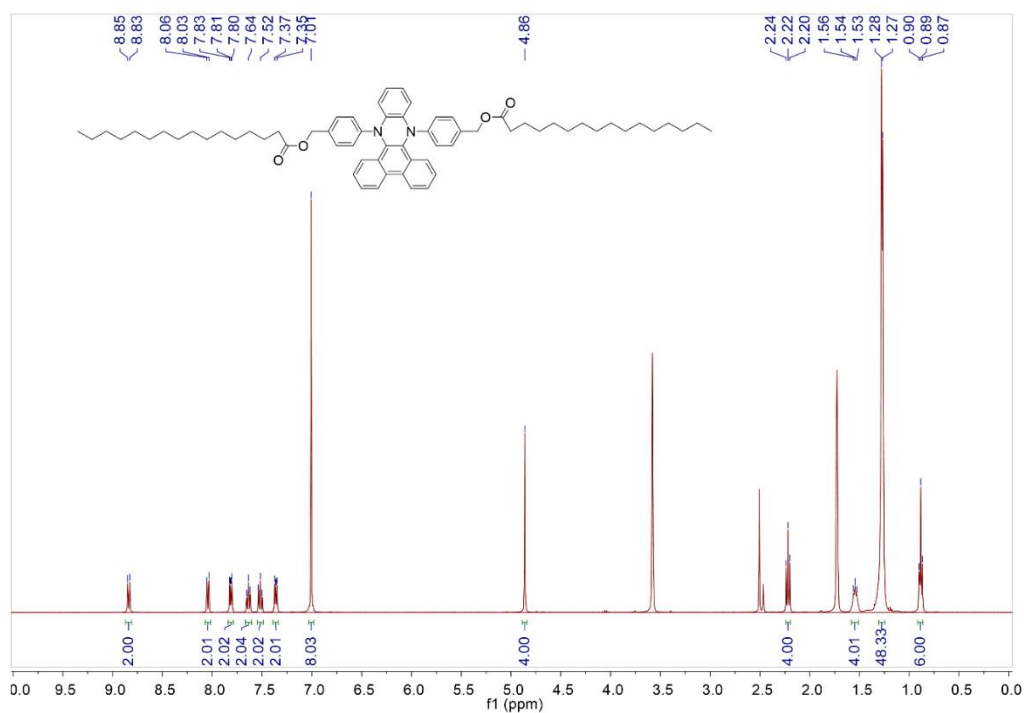
1: TOF MS ES+
1.28e+004

Figure S6. HRMS spectrum of DPAC-10.

Figure S7. ^1H NMR spectrum of DPAC-15 in THF-d_8 .

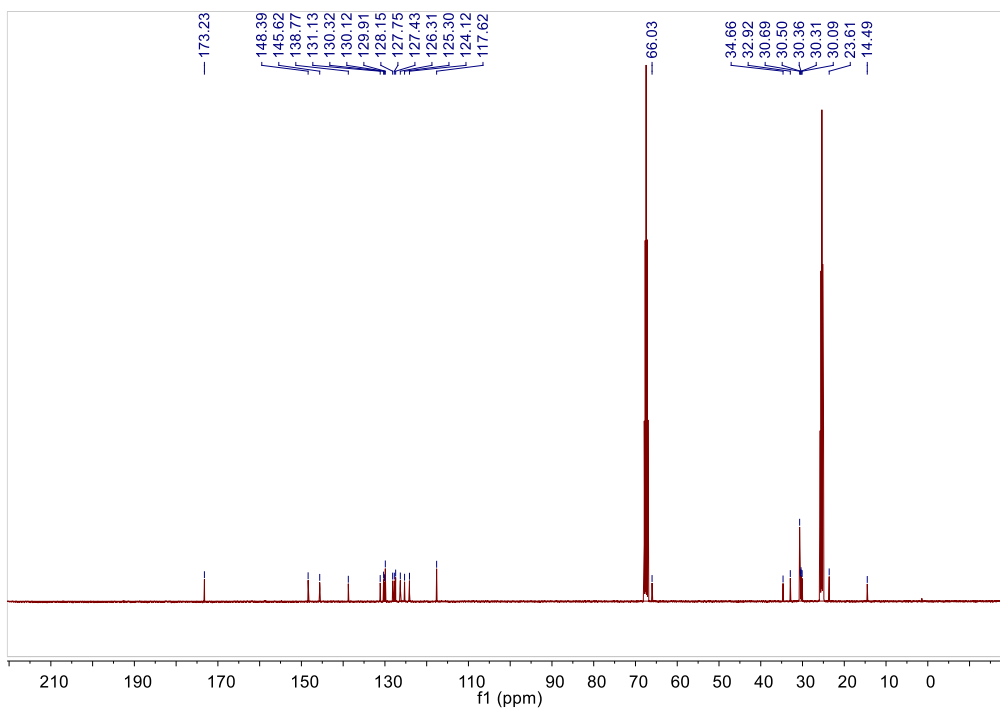


Figure S8. ^{13}C NMR spectrum of DPAC-15 in $\text{THF-}d_8$.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

16 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

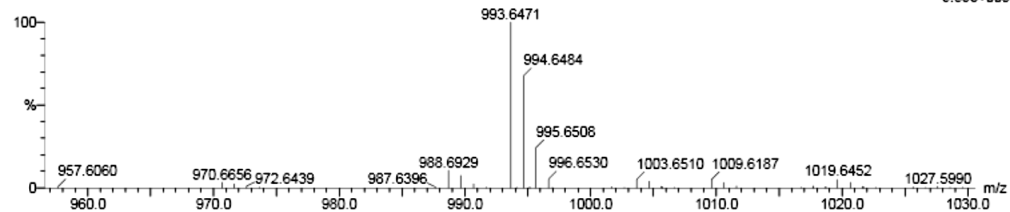
Elements Used:

C: 0-66 H: 0-86 N: 0-2 O: 0-4 Na: 0-1

H-TIAN

TH-LH-10 158 (1.809) Cm (156:158)

1: TOF MS ES+
9.39e+003



Minimum:

Maximum:

5.0 10.0 -1.5
50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
993.6471	993.6485	-1.4	-1.4	24.5	37.4	0.0	C66 H86 N2 O4 Na

Figure S9. HRMS spectrum of DPAC-15.

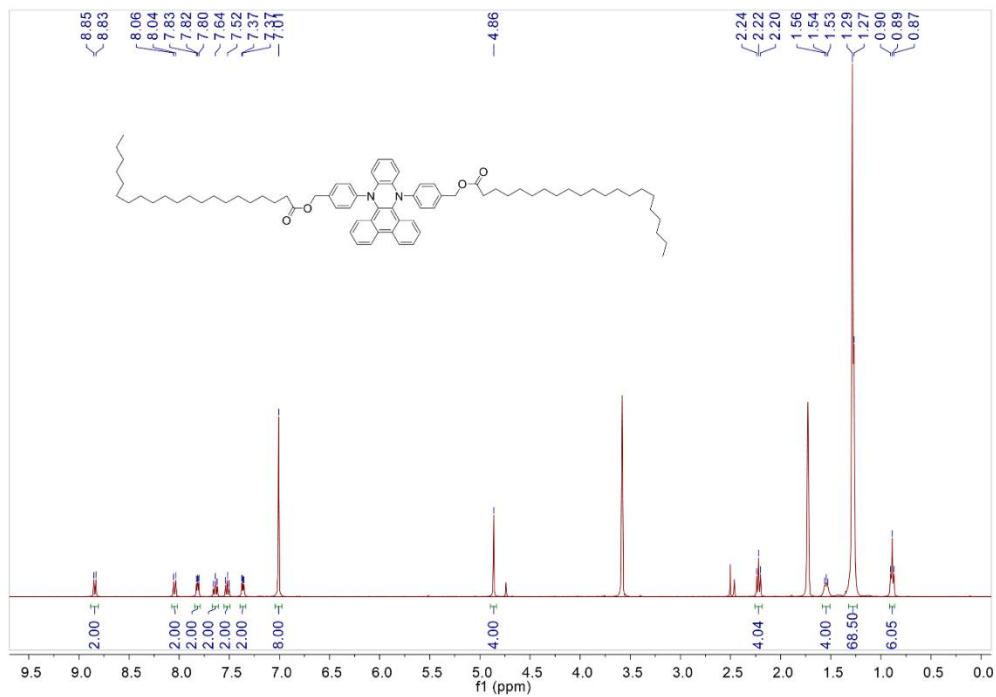


Figure S10. ^1H NMR spectrum of DPAC-20 in $\text{THF-}d_8$.

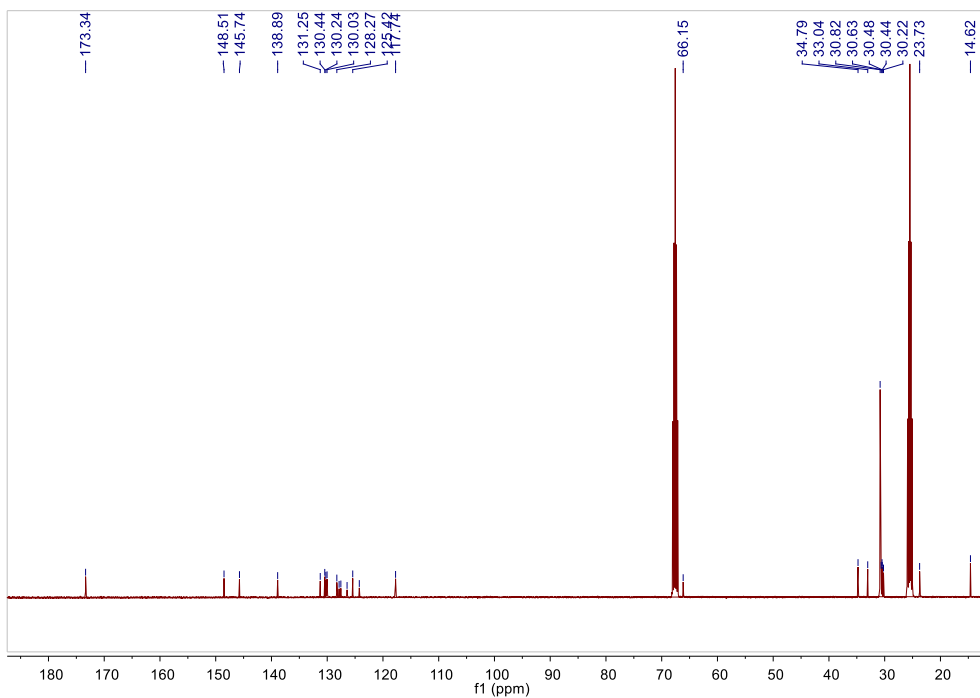


Figure S11. ^{13}C NMR spectrum of DPAC-20 in $\text{THF-}d_8$.

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

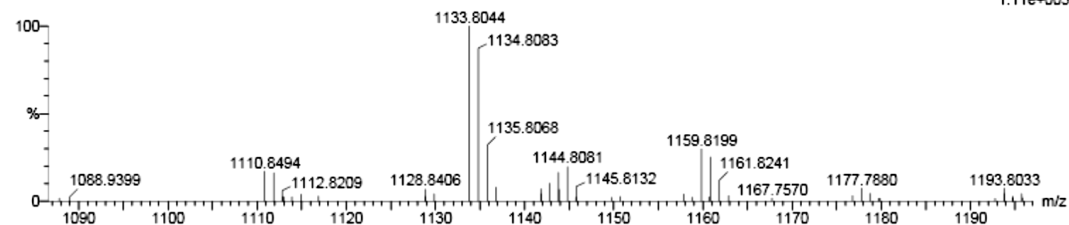
16 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-76 H: 0-106 N: 0-2 O: 0-4 Na: 0-1

H-TIAN

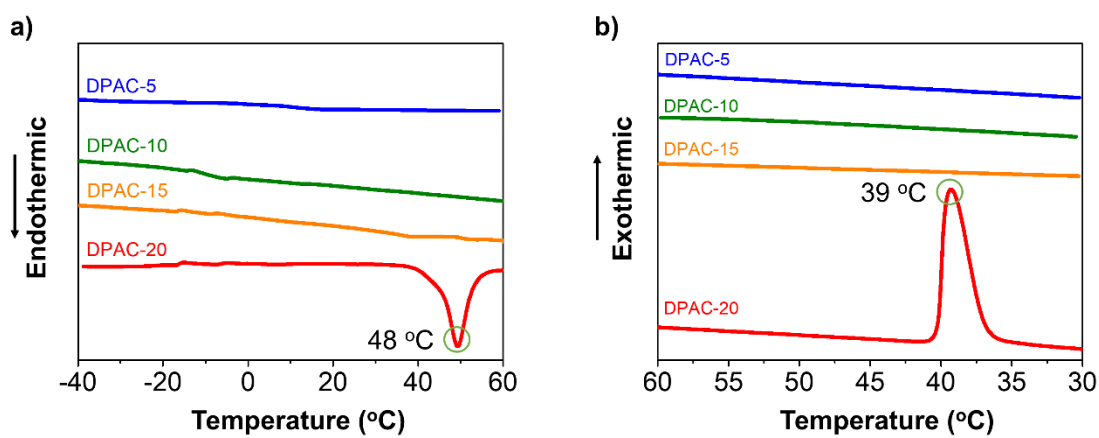
TH-LH-11 74 (0.841) Cm (74.76)

1: TOF MS ES+
1.11e+003

Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1133.8044	1133.8050	-0.6	-0.5	24.5	12.1	0.0	C76 H106 N2 O4 Na

Figure S12. HRMS spectrum of DPAC-20.

Figure S13. DSC thermograms of the DPAC-*n* compounds in the a) heating and b) cooling courses.

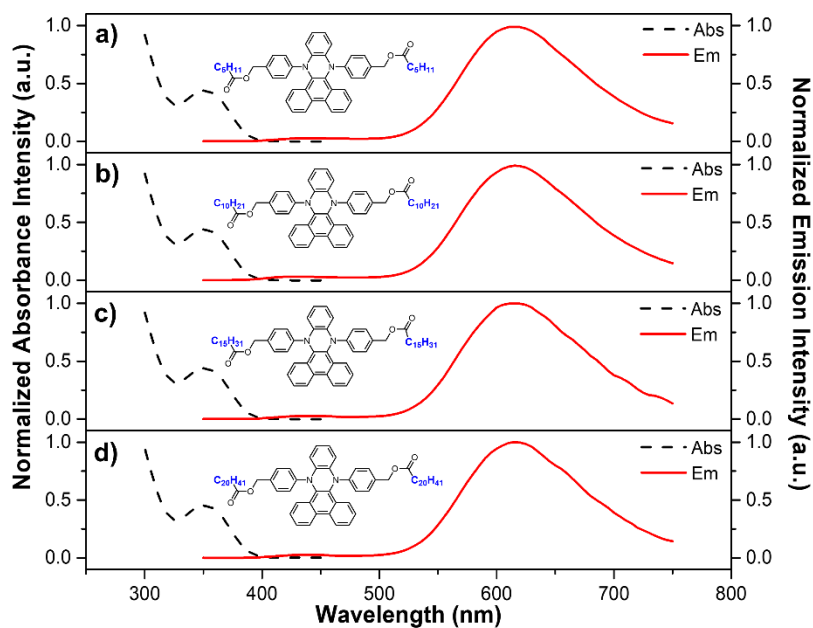


Figure S14. Absorption (black lines) and emission (red lines) spectra of (a) DPAC-5, (b) DPAC-10, (c) DPAC-15, and (d) DPAC-20 in dichloromethane (10^{-5} M) (excited at 365 nm).

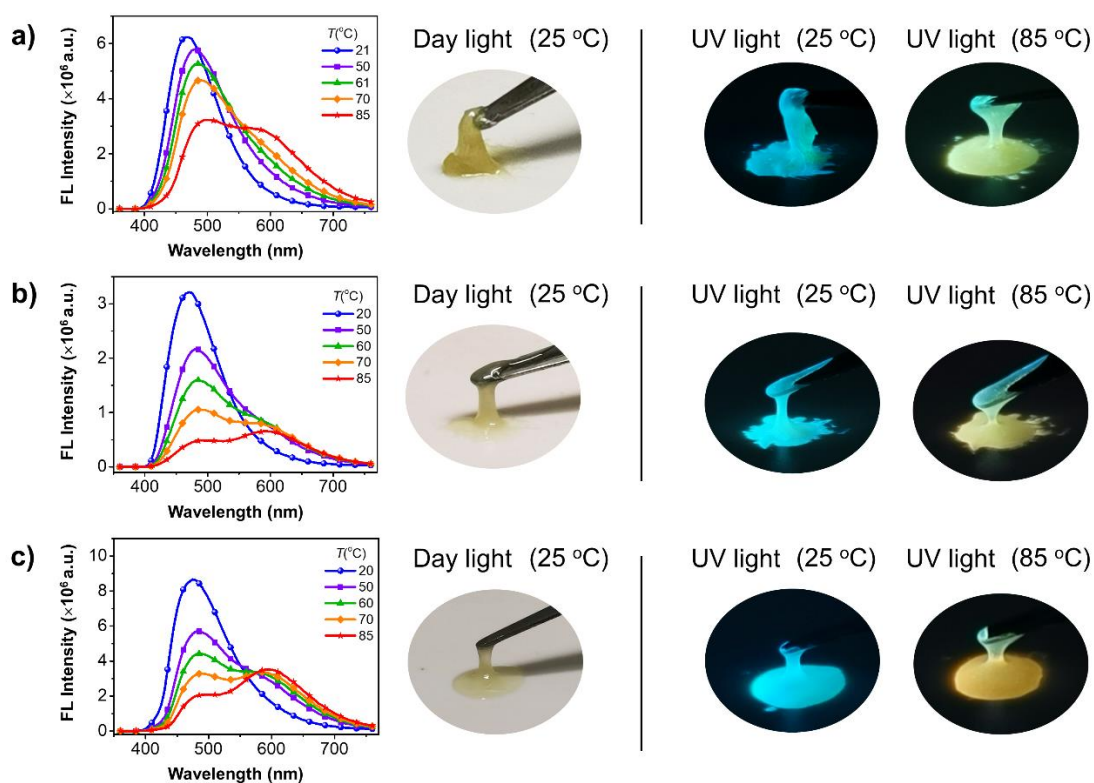


Figure S15. Fluorescence spectra of DPAC-*n* derivatives when the temperature varies from 20 to 85 °C, and the images under the daylight (left) at 25 °C and 365 nm UV light at 25 °C (middle) and 85 °C (right) of the solvent-free liquids of a) DPAC-5, b) DPAC-10, and c) DPAC-15.

Table S2. Quantum yields of four compounds at 20 °C, and 85 °C.

Temperature	Quantum yield (%)			
	DPAC-5	DPAC-10	DPAC-15	DPAC-20
20 °C	77.8	80.1	81.4	82.2
85 °C	61.9	54.4	52.4	45.3

Note: The fluorescence quantum yields of all the DPAC-*n* derivatives were tested using HAMAMATSU Quantaurus-QY C11347-11. Since the instrument for the measurement of fluorescence quantum yields cannot directly heat samples, we heated the samples using an external heater. Each sample was heated to 85 °C and kept at this temperature for 10 minutes, and afterwards was quickly put into the sample cell of HAMAMATSU Quantaurus-QY C11347-11 for testing. The fluorescence quantum yields were acquired point by point as the temperature decreased from 85 to 20 °C. Each measurement was repeated for three times.

Table S3. CIE coordinates of DPAC-*n* from 20 °C to 85 °C

<i>T</i> (°C)	CIE coordinates (<i>x</i> , <i>y</i>)			
	DPAC-5	DPAC-10	DPAC-15	DPAC-20
20	(0.18, 0.24)	(0.18, 0.25)	(0.21, 0.30)	(0.18, 0.24)
25	(0.19, 0.25)	(0.19, 0.26)	/	/
30	(0.19, 0.27)	(0.20, 0.28)	(0.23, 0.32)	(0.19, 0.26)
35	(0.20, 0.28)	(0.21, 0.30)	(0.25, 0.34)	/
49	(0.21, 0.30)	(0.23, 0.31)	(0.26, 0.35)	(0.20, 0.27)
45	(0.22, 0.31)	(0.24, 0.33)	(0.27, 0.36)	(0.26, 0.34)
50	(0.23, 0.33)	(0.25, 0.34)	(0.29, 0.37)	(0.32, 0.38)
55	(0.24, 0.34)	(0.27, 0.35)	(0.30, 0.38)	(0.34, 0.39)
60	(0.26, 0.36)	(0.29, 0.37)	(0.33, 0.39)	(0.36, 0.40)
65	(0.27, 0.37)	(0.31, 0.38)	(0.34, 0.40)	(0.38, 0.41)
70	(0.28, 0.38)	(0.32, 0.38)	(0.36, 0.41)	(0.40, 0.41)
75	(0.30, 0.40)	(0.34, 0.39)	(0.38, 0.41)	(0.42, 0.42)
80	(0.32, 0.41)	(0.36, 0.40)	/	(0.43, 0.42)
85	(0.35, 0.42)	(0.39, 0.41)	(0.42, 0.42)	(0.45, 0.43)

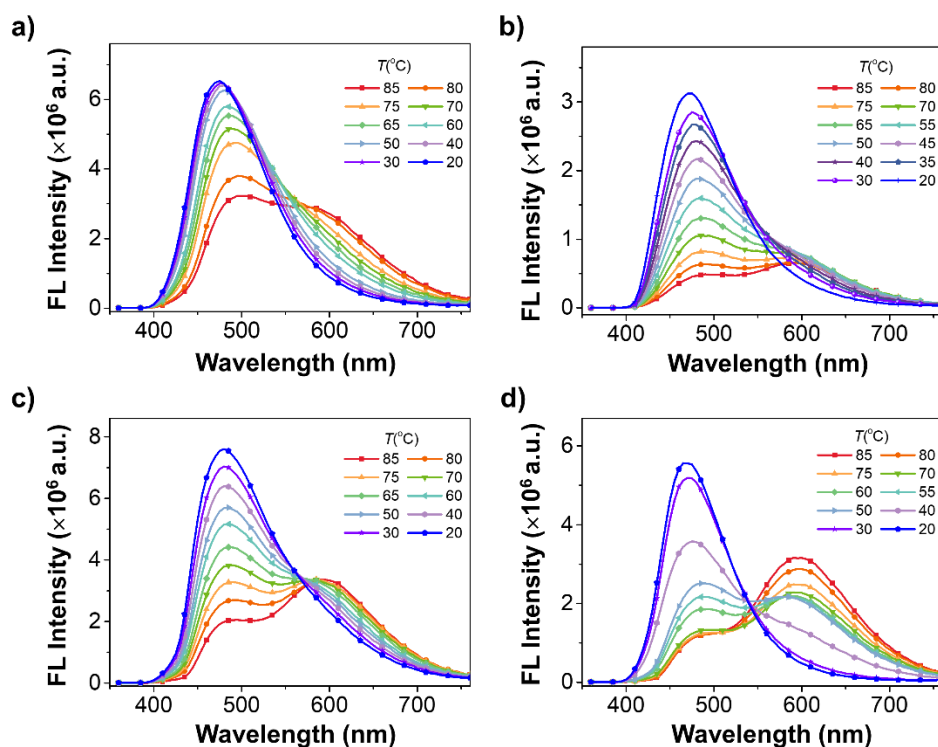


Figure S16. Fluorescence spectra recorded during the cooling process from 85 °C to 20 °C of a) DPAC-5, b) DPAC-10, c) DPAC-15, and d) DPAC-20.

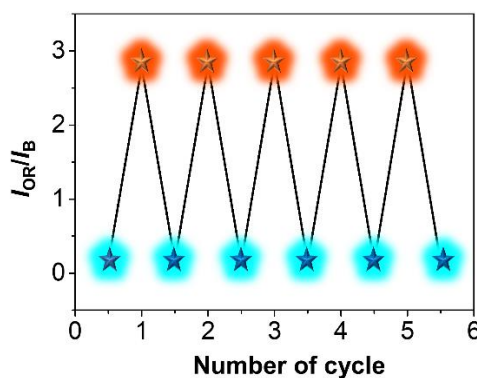


Figure S17. Reversible change in I_{OR}/I_B of DPAC-20 upon cycling the temperature five times between 40 °C and 85 °C. The “red stars” stand for the predominate orange-red fluorescence of DPAC-20 at 85 °C, while the “cyan stars” represent the dominant blue fluorescence at 40 °C.

S1 J. Li, M. Tian, H. Xu, X. Ding and J. Guo, *Part. Part. Syst. Charact.*, 2019, **36**, 1900346.

S2 X. Li, Y. Xie, B. Song, H. L. Zhang, H. Chen, H. Cai, W. Liu and Y. Tang, *Angew. Chem. Int. Ed.*, 2017, **56**, 2689-2693.