Supplementary Information

Heterocyclic compounds bearing s-triazine and cyclotriphosphazene scaffold: facile synthesis, hydrogen-bonded organic frameworks construction and fluorescent amine sensing

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Supplementary Index

Materials and Instrumentations

All starting materials were of reagent grade quality and were obtained from commercial sources without further purification. The powder X-ray diffraction pattern (PXRD) was obtained on an Advance-D8 equipped with Cu-Kα radiation in the range $5° < 2\theta < 55°$, with a step size of 0.02° (2θ) and a count time of 2 s/step at room temperature. All IR measurements were obtained using a Bruker AXS TENSOR-27 FT-IR spectrometer with pressed KBr pellets in the range of 400–4000 cm^{-1} at room temperature. Elemental analyses for C, H and N were measured on a Model 240C automatic Perkin-Elmer elemental analyzer. UV-vis-NIR spectra were recorded on a JASCO V-570

UV/vis/NIR microspectrophotometer (200-2500 nm). Fluorescence spectra were measured on a JASCO FP-4600 and HORIBA Fluoromax-4-TCSPC fluorimeter. Liquid UV-visible absorption spectroscopy was performed on SPECORD 250/PLUS.

X-ray Crystallography Determination

Suitable single crystal of the HOF-TRIPOD and HOF-HAPCP were mounted on glass fibers for X-ray measurement. Reflection data was collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å).[s-1] All the measured independent reflections ($I > 2\sigma(I)$) were used in the structural analyses, and semi-empirical absorption corrections were applied using the SADABS program.[s-2] All calculations were performed using the SHELXS-2017 program[s-3] and refined by full-matrix least-squares techniques using the SHELXL-2017 program.[s-4] All non-hydrogen atoms were refined anisotropically. Restraints in bond length and thermal parameters were applied to the disordered part in HOF-TRIPOD. The disordered guest molecules in HOF-TRIPOD which cannot be modelled were treated by the SQUEEZE routine. Analysis of the residual electron density using the SQUEEZE function within the PLATON programs indicates the presence of 28 electrons per formula unit, this corresponds to 0.875 molecules of acetone as counter molecular based on charge balance, which were defined by considering the solvent composition results. The details of the crystal parameters, data collection, and refinement for HOF-TRIPOD and HOF-HAPCP are summarized in Table S1 and Table S2, and selected bond lengths and bond angle are listed in Table S3 and Table S4.

The synthetic route of 2, 4, 6-tris(p-formylphenoxy)-1, 3, 5-triazine (TRIPOD)

p-Hydroxybenzaldehyde (5.5 g, 45 mmol), sodium hydroxide (1.8 g, 45 mmol), acetone (20 mL) and water (20 mL) were added to a 250 mL two-necked flask, it was continuously stirred in an ice-water bath until dissolved. After about 30 min, cyanuric chloride (2.75 g, 15 mmol) and acetone (100 mL) was added dropwise to the two-necked flask using a constant pressure dropping funnel under the protection of N2. After about 1 h, the reaction flask was refluxed for 6 h at 72°C. Then the reacted product was suction filtered, and it was washed with distilled water until neutral. The obtained white filter cake was air-dried at room temperature (25 ℃) to obtain the target product TRIPOD. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 3H), 7.94 (d, *J*=8.6 Hz, 6H), δ=7.34 (d, *J*=8.6 Hz, 6H).

The synthetic route of (6-aldehyde phenoxy) cyclotriphosphazene (HAPCP)

(The whole process was carried out under the protection of N_2, and anhydrous potassium carbonate was dried in an oven at 120 ℃ for 2 h).

Cyanuric cyanurate (1.00 g, 2.88 mmol), potassium carbonate (5.17 g, 37.41 mmol), and tetrahydrofuran (THF, 15 mL) were added in a 100 mL flask, and the mixture was stirred in an ice-water bath for 30 min. P-hydroxybenzaldehyde (2.46 g, 20.14 mmol) was dissolved in a THF (10 mL) solution, and slowly added it dropwise to the flask (about 30 min). After the addition was completed, the reaction was refluxed at 74 ℃ for 24 h. After the reaction, the turbid substance in the bottle was rotary steamed. After the solvent was evaporated, the solid was dissolved in water to wash off the potassium carbonate, the filter cake was washed with ethanol and dried to obtain a crude product.

Then it was recrystallized for 2 h, and the filter cake was washed with ethanol and

dried to obtain the target product HAPCP. ^{1}H-NMR (400 MHz, $CDCl_3$)：δ 9.96 (s, 6H), 7.76 (d, *J*=8.6 Hz, 12H), 7.17 (d, *J*=8.6 Hz, 12H).

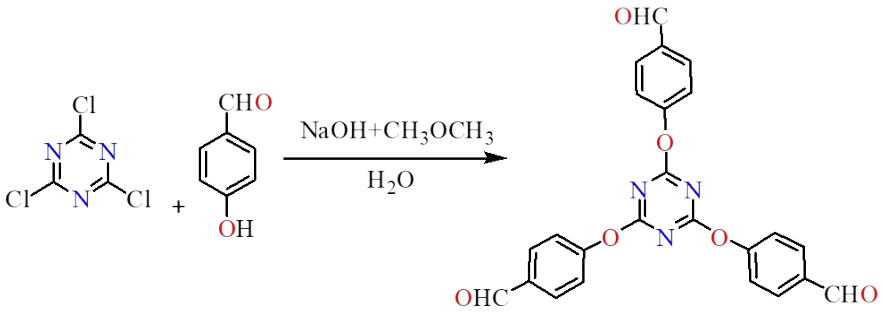

Figure S1. Synthetic route of TRIPOD.

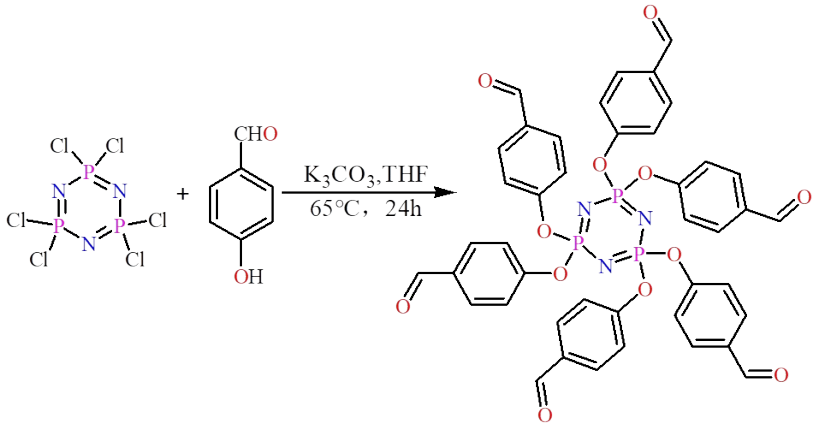

Figure S2. The synthetic route of HAPCP.

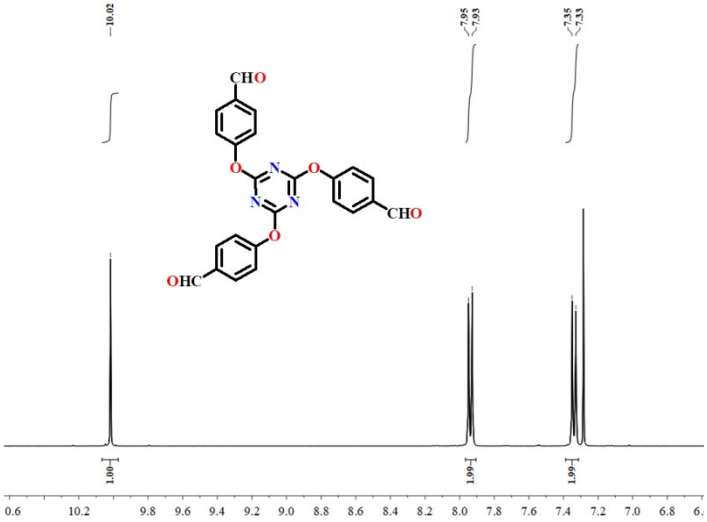

Figure S3. ^{1}H-NMR spectrum of the ligand TRIPOD.

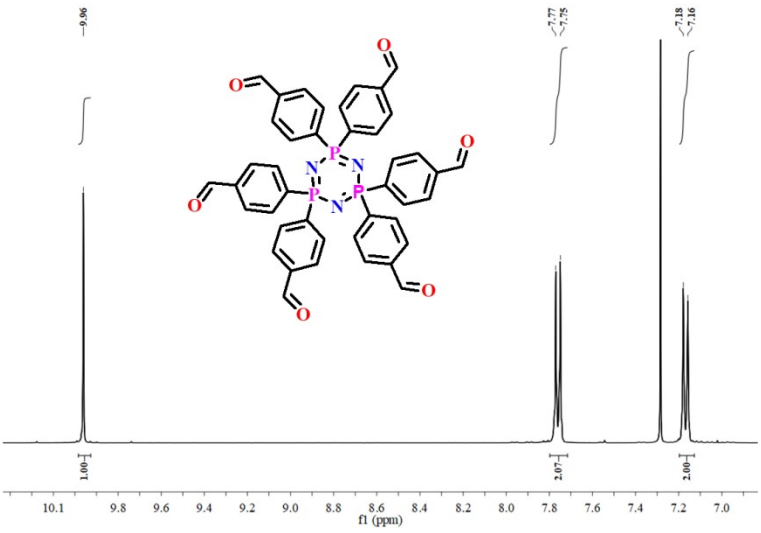

Figure S4. ^{1}H-NMR spectrum of the ligand HAPCP.

Table S1. The crystallographic data for HOF-TRIPOD and HOF-HAPCP.

	HOF-TRIPOD	**HOF-HAPCP**
Formula	$C_{24}H_{15}N_3O_6$	$C_{42}H_{30}N_3O_{12}P_3$
Molecular weight	441.39	861.60
Crystal system	Trigonal	Orthorhombic
Space group	*R*-3	$P2_12_12_1$
a/Å	14.5753(7)	7.9006(11)
b/Å	14.5753(7)	14.2403(19)
c/Å	20.6709(19)	35.402(5)
α/(°)	90	90
β/(°)	90	90
γ (°)	120	90
V (Å^3)	3803.0(5)	3982.9(9)
Z	6	4
D_{calc}/(g·cm^{-3})	1.156	1.437
F(ooo)	1368.0	1776.0
μ/mm^{-1}	0.085	0.219
2θ range/(°)	3.78-56.546	2.3-56.542
Reflections collected	8211	25579

Independent reflections [I>2σ(*I*)]	2109	9744
Parameters	110	542
Goodness of fit	1.094	1.048
R[a]	0.0523(0.0880)[b]	0.0650(0.1053)[b]
wR_2[a]	0.1831(0.2090)[b]	0.1749(0.2017)[b]
Δ(*ρ*) (e Å^{-3})	0.16 and -0.19	0.62 and -0.41

[*a]$R=\Sigma||Fo|-|Fc||/\Sigma|Fo|$, $wR_2=[\Sigma w(Fo^2-Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$; [$Fo>4\sigma(Fo)$]. [b]Based on all data.

Table S2. H-bond interactions in HOF-TRIPOD.

D-H···A	d(D-H)(Å)	d(H···A)(Å)	d(D···A)(Å)	<(DHA)(°)
C4-H4···O2[#1]	0.93	2.48	3.320(4)	150.2

#1: y+2/3, -x+y+1/3, -z+1/3

Table S3. H-bond interactions in HOF-HAPCP.

D-H···A	d(D-H)(Å)	d(H···A)(Å)	d(D···A)(Å)	<(DHA)(°)
C9-H9···O4	0.93	2.57	3.465(8)	161.6
C34-H34···N3	0.93	2.70	3.333(9)	126.3
C16-H16···O12[#1]	0.93	2.70	3.355(9)	128.0
C23-H23···O11[#2]	0.93	2.58	3.245(10)	129.0
C26-H26···O10[#3]	0.93	2.72	3.358(14)	126.5
C28-H28···O9[#4]	0.93	2.52	3.372(15)	151.9
C31-H31···O8[#5]	0.93	2.79	3.437(11)	127.7

#1: -x, y+1/2, -z+1/2; #2: -x+1, y+1/2, -z+1/2; #3: x, y+1, z; #4: x+1/2, -y+5/2, -z; #5: -x+1, y-1/2, -z+1/2.

Table S4. The selected bond distances (Å) and bond angles (°) of HOF-TRIPOD.

O(1)-C(1)	1.340(19)	C(2)-C(4)	1.366(3)

O(1)-C(2)	1.406(2)	C(3)-C(5)	1.381(3)
O(2)-C(8)	1.141(4)	C(4)-C(6)	1.371(3)
N(1)-C(1)	1.314(2)	C(5)-C(7)	1.386(3)
N(1)-C(1)$^{\#1}$	1.333(2)	C(6)-C(7)	1.352(3)
C(2)-C(3)	1.356(3)	C(7)-C(8)	1.475(3)
C(1)-O(1)-C(2)	118.9(12)	C(2)-C(3)-C(5)	118.1(2)
C(1)-N(1)-C(1) $^{\#1}$	112.3(15)	C(6)-C(4)-C(2)	119.1(2)
N(1) $^{\#2}$-C(1)-O(1)	112.7(14)	C(3)-C(5)-C(7)	120.8(2)
N(1)-C(1)-O(1)	119.6(14)	C(4)-C(6)-C(7)	120.8(2)
N(1)-C(1)-N(1) $^{\#2}$	127.7(15)	C(5)-C(7)-C(8)	120.7(3)
C(3)-C(2)-O(1)	117.8(17)	C(6)-C(7)-C(5)	119.2(2)
C(3)-C(2)-C(4)	122.0(18)	C(6)-C(7)-C(8)	120.1(3)
C(4)-C(2)-O(1)	120.1(18)	O(2)-C(8)-C(7)	128.8(4)

Table S5. The selected bond distances (Å) and bond angles (°) of HOF-HAPCP.

O(5)-C(1)	1.390(7)	C(1)-C(2)	1.398(9)
O(10)-C(7)	1.090(12)	C(3)-C(2)	1.380(11)
O(6)-C(8)	1.392(7)	C(4)-C(5)	1.366(10)
N(1)-P(1)	1.581(5)	C(5)-C(6)	1.412(10)
N(1)-P(2)$^{\#1}$	1.580(5)	C(7)-C(4)	1.550(14)
N(2)-P(1)	1.580(5)	C(9)-C(10)	1.368(9)
C(6)-C(1)-C(2)	121.7(6)	N(1)-P(1)-O(3)	109.6(2)
P(2)-N(1)-P(1)	121.4(3)	N(2)-P(1)-N(1)	117.4(3)
P(1)-N(2)-P(3)	121.5(3)	O(4)-P(1)-N(1)	112.0(2)
P(3)-N(3)-P(2)	121.6(3)	O(4)-P(1)-O(3)	99.6(2)
C(15)-O(1)-P(2)	123.6(4)	N(1)-P(2)-O(1)	110.9(2)
C(29)-O(2)-P(2)	124.6(4)	N(3)-P(3)-O(6)	111.1(3)
C(36)-O(3)-P(1)	121.8(4)	O(6)-P(3)-N(2)	110.9(3)
C(1)-O(5)-P(3)	128.1(4)	O(6)-P(3)-O(5)	99.0(2)

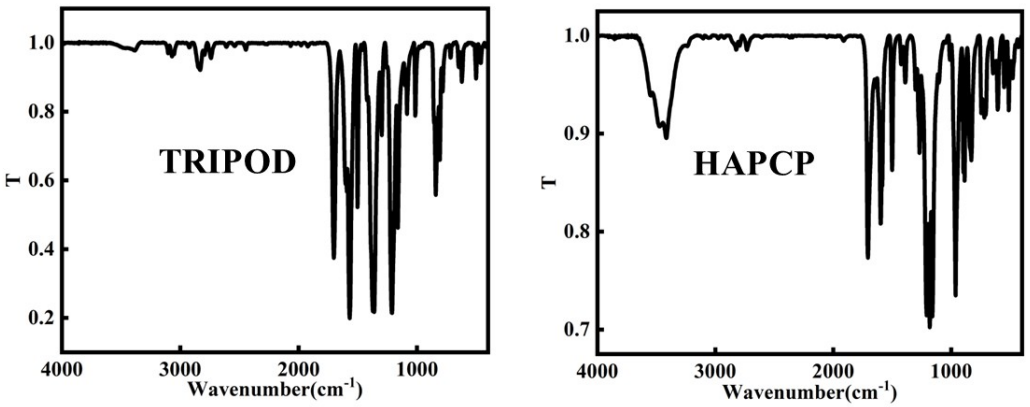

Figure S5. The IR spectra of TRIPOD and HAPCP.

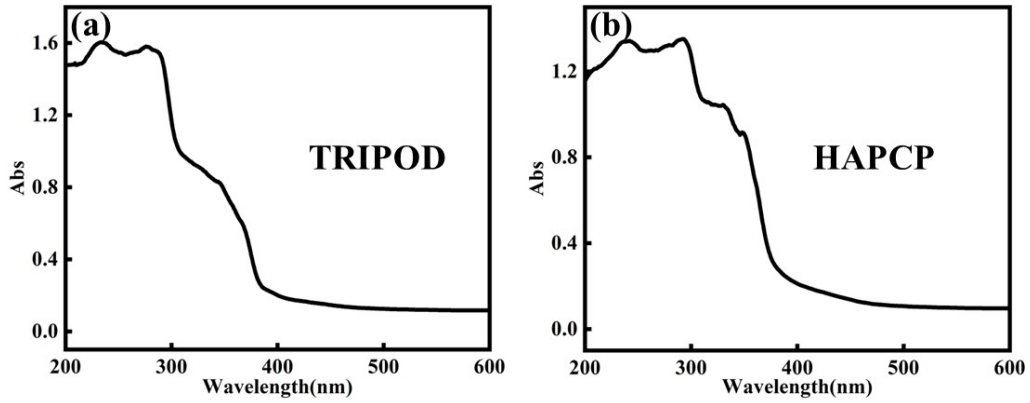

Figure S6. The UV spectra of (a)TRIPOD; (b)HAPCP.

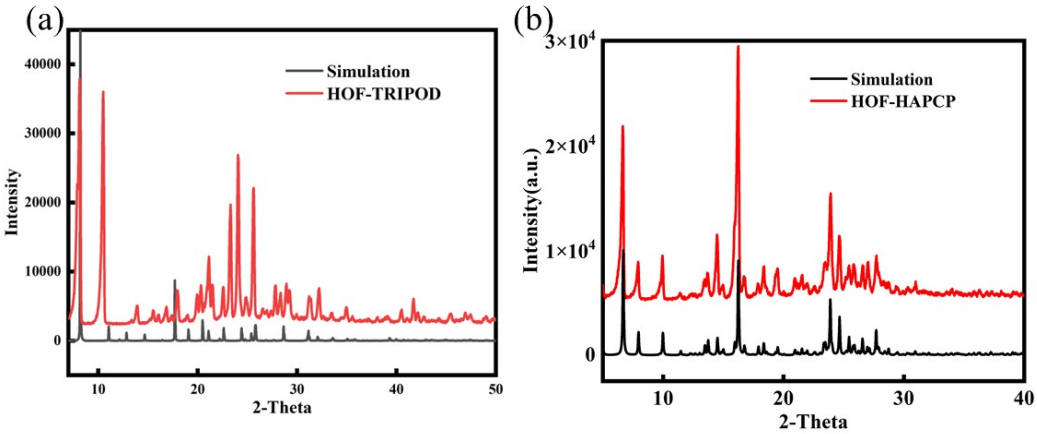

Figure S7. PXRD patterns for HOF-TRIPOD and HOF-HAPCP.

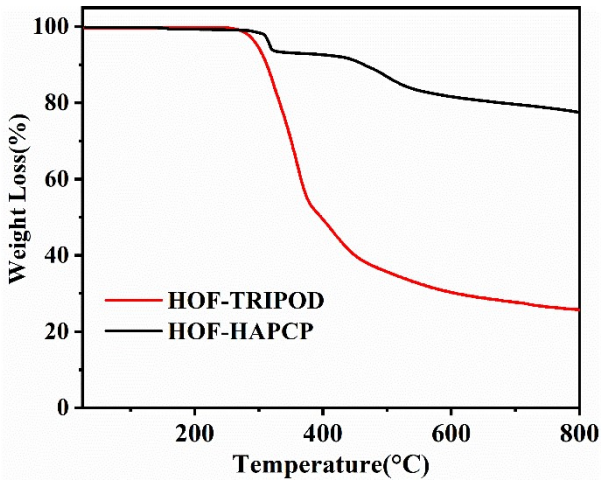

Figure S8. Thermogravimetric curves of HOF-TRIPOD and HOF-HAPCP.

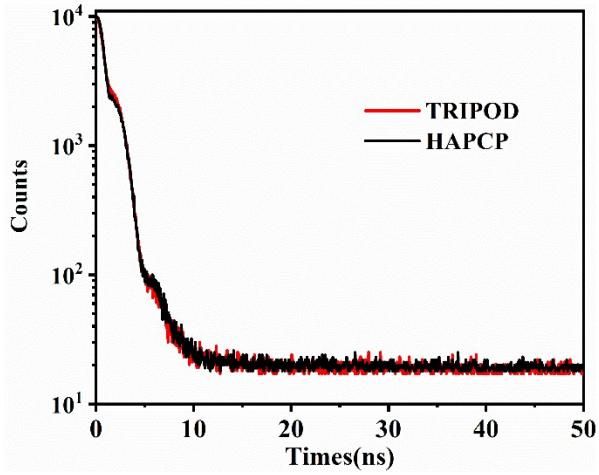

Figure S9. Fluorescence decay profiles of TRIPOD and HAPCP in solid state.

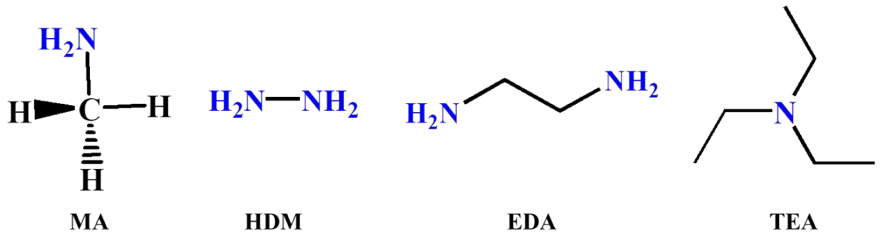

Figure S10. Structures of the aliphatic amine.

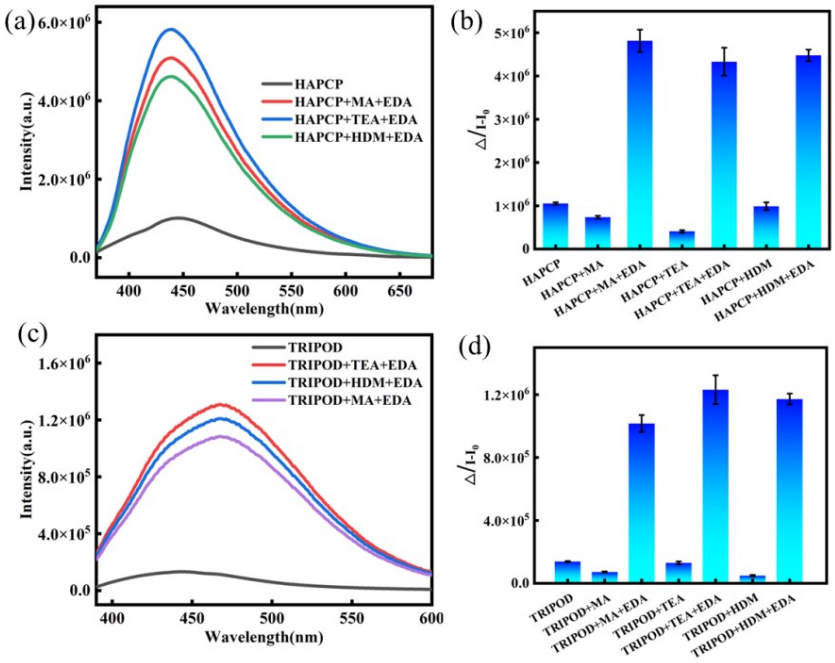

Figure S11. Fluorescence intensity changes after adding different fatty amines: (a, b) HAPCP; (c, d) TRIPOD.

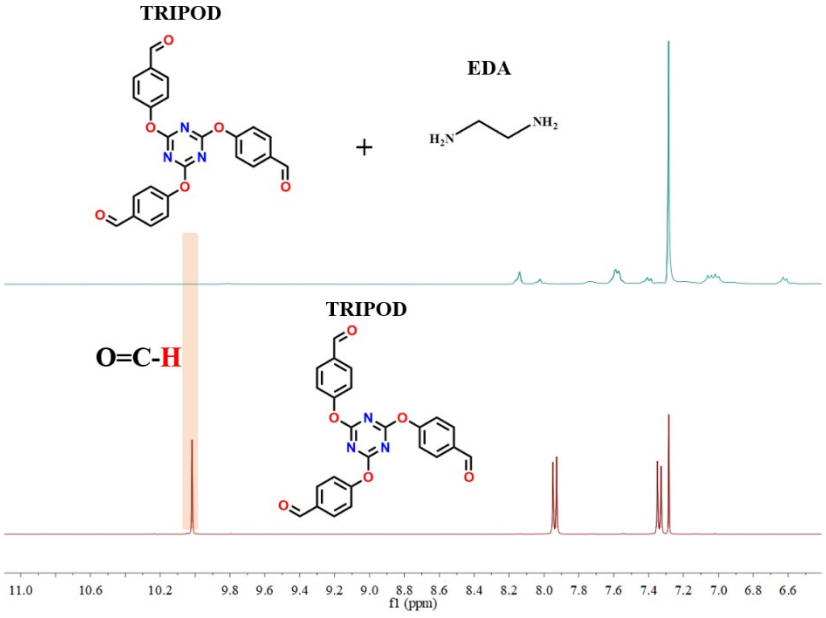

Figure S12. ^{1}H-NMR spectrum of TRIPOD and TRIPOD@EDA in $CDCl_3$.

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