Supporting Information for

Three-in-One: information encryption, anti-counterfeiting and LDs-tracking of multifunctional purine derivatives

Hao-Yuan Wang[a], Kang-Kang Yu[a,b*], Chong-Yun Tan[a], Kun Li[a], Yan-Hong Liu[a], Lei Shi[a], Kai Lu[a], Xiao-Qi Yu[a*]

[a] Key Laboratory of Green Chemistry and Technology (Ministry of Education), College of Chemistry, Sichuan University, Chengdu, 610064, China.

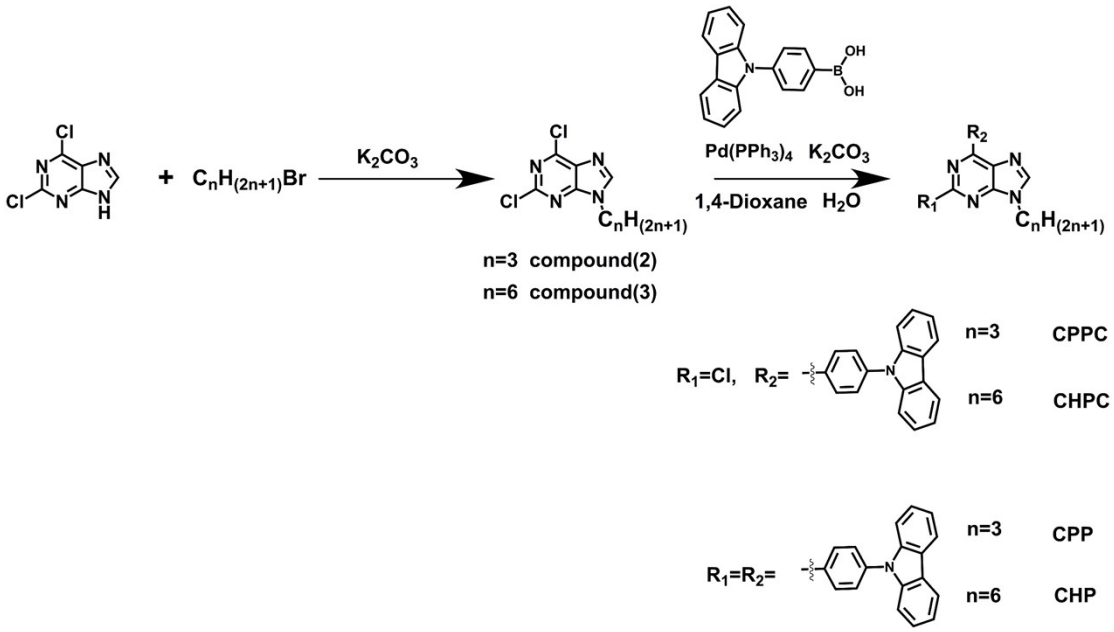
Email: xqyu@scu.edu.cn

[b] Key Laboratory of Bio-resources and Eco-environment (Ministry of Education), College of Life Sciences, Sichuan University, Chengdu, 610064, China.

E-mail: kangkangyu@scu.edu.cn

Experimental Section

Reaction procedures[1,2]



Scheme S1. The synthetic routes for **CPPC**, **CHPC**, **CPP** and **CHP**

2,6-dichloro-9-hexyl-9H-purine (**3**)

Compound 3 was produced using the same procedure as **compound 2** by changing the 1-bromopropane as 1-Bromohexane. Compound 3 was obtained as white solid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 8.09 (s, 1H, a-H), 4.22 (t, J = 7.3 Hz, 2H, b-H), 1.86 (m, 2H, c-H), 1.26 (s, 6H, (d-f)-H), 0.81 (t, J = 6.8 Hz, 3H, g-H). HRMS (ESI): m/z: Calcd for $C_{11}H_{15}C_{l2}N_4^+$: 273.0674 $[M+H]^+$; Found: 273.0628.

9-(4-(2-chloro-9-hexyl-9H-purin-6-yl)phenyl)-9H-carbazole (**CHPC**)

The synthesis and purification of **CHPC** were similar to that of **CPPC** but with Compound **2** instead of Compound **3**. Compound **CHPC** was obtained as a yellowish solid in 70 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 9.03 (d, J = 8.8 Hz,

2H, j, k-H or l, m-H), 8.14 (d, J = 7.2 Hz, 2H, h-H and i-H), 8.13 (s, 1H, a-H), 7.79 (d, J = 8.9 Hz, 2H, j, k-H or l, m-H), 7.53 (d, J = 8.2 Hz, 2H, n-H and o-H), 7.44-7.40 (m, 2H, q-H and p-H), 7.32-7.28 (m, 2H, r-H and s-H), 4.30 (t, J = 7.3 Hz, 2H, b-H), 1.95 (m, 2H, c-H), 1.35 (m, 6H, (c-f)-H), 0.91-0.85 (m, 3H, g-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 155.46, 154.31, 154.24, 145.07, 140.73, 140.34, 133.21, 131.63, 130.10, 126.74, 126.12, 123.69, 120.37, 109.92, 44.20, 31.16, 29.81, 26.31, 22.46, 13.96.HRMS (ESI): m/z: Calcd for $C_{29}H_{27}ClN_5^+$: 480.1955 $[M+H]^+$; Found: 480.1955.

9,9'-((9-propyl-9H-purine-2,6-diyl)bis(4,1-phenylene))bis(9H-carbazole) (**CPP**)

The synthesis and purification of **CPP** were similar to that of **CPPC**, but the input proportion of Compound **2** and (4-(9H-Carbazol-9-yl)phenyl)boronic acid was change from 1.2:1 to 1:2.2. Compound **CPP** was obtained as a white solid in 49 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 9.22 (d, J = 8.6 Hz, 2H, g_1-j_1-H or g_2-j_2-H), 8.94 (d, J = 8.5 Hz, 2H, g_1-j_1-H or g_2-j_2-H), 8.19 (s, 1H, a-H), 8.16 (d, J = 7.8 Hz, 4H, e_1-H, e_2-H, f_1-H and f_2-H), 7.84 (d, J = 8.6 Hz, 2H, g_1-j_1-H or g_2-j_2-H), 7.76 (d, J = 8.5 Hz, 2H, g_1-j_1-H or g_2-j_2-H), 7.59-7.53 (m, 4H, k_1-H, k_2-H, l_1-H, and l_2-H), 7.44 (d, J = 15.4 Hz, 4H, m_1-H, m_2-H, n_1-H and n_2-H), 7.31 (t, J = 7.5 Hz, 4H, o_1-H, o_2-H, p_1-H and p_2-H), 4.42 (d, J = 7.1 Hz, 2H, b-H), 2.11 (q, J = 7.3 Hz, 2H, c-H), 1.08 (t, J = 7.4 Hz, 3H, d-H).^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 157.90, 153.76, 153.34, 144.81, 140.65, 140.51, 140.04, 139.33, 137.30, 134.91, 131.39, 129.95, 129.88, 126.82, 126.07, 126.01, 123.62, 123.53, 120.35, 120.22, 120.09, 109.97, 109.91, 45.65, 23.35, 11.40. HRMS (ESI): m/z: Calcd for $C_{44}H_{33}N_6^+$: 645.2767 $[M+H]^+$; Found: 645.2725.

9,9'-((9-propyl-9H-purine-2,6-diyl)bis(4,1-phenylene))bis(9H-carbazole) (**CHP**)

The synthesis and purification of **CHP** were similar to that of **CPP**, but with Compound **2** instead of Compound **3**. Compound **CHP** was obtained as a white solid in 63 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 9.23 (d, J = 8.6 Hz, 2H, j_1-m_1 or j_2-m_2), 8.94 (d, J = 8.6 Hz, 2H, j_1-m_1 or j_2-m_2), 8.18-8.16 (m, 5H, i_1-H, i_2-H, h_1-H, h_2-H and a-H (8.17)), 7.85 (d, J = 8.6 Hz, 2H, j_1-m_1 or j_2-m_2), 7.77 (d, J = 8.6 Hz, 2H, j_1-m_1 or j_2-m_2), 7.59-7.54 (m, 4H, o_1-H, o_2-H, n_1-H and n_2-H), 7.46-7.42 (m, 4H, p_1-H, p_2-H, q_1-H and q_2-H), 7.33-7.30 (m, 4H, r_1-H, r_2-H, s_1-H and s_2-H), 4.42 (t, J = 7.2 Hz, 2H, b-H), 2.06 (m, 2H, c-H), 1.46-1.31 (m, 6H, (d-f)-H), 0.91 (t, J = 7.1 Hz, 3H, g-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 1157.89, 153.74, 153.33, 144.79, 140.66, 140.52, 140.04, 139.34, 137.31, 134.93, 131.40, 129.94, 129.89, 126.83, 126.09, 126.03, 123.63, 123.54, 120.37, 120.24, 120.10, 109.98, 109.93, 43.95, 31.22, 29.93, 26.42, 22.52, 14.02. HRMS (ESI): m/z: Calcd for $C_{47}H_{39}N_6^+$: 687.3236 $[M+H]^+$; Found: 687.3222.

Information encryption process

A clean 96-well plate was used for demonstrating the encryption scheme. For example, to paint the encrypted message "SCU" on the plate, the selected wells were injected with 200 μL of ethanol (solution I). Then, remaining wells were injected with 200 μL of water (solution II) to achieve information encryption. When all wells were injected with 0.2 μL compound solution (5mM, DMF), and the plate was gently shaken, the information was displayed in 365 UV light.

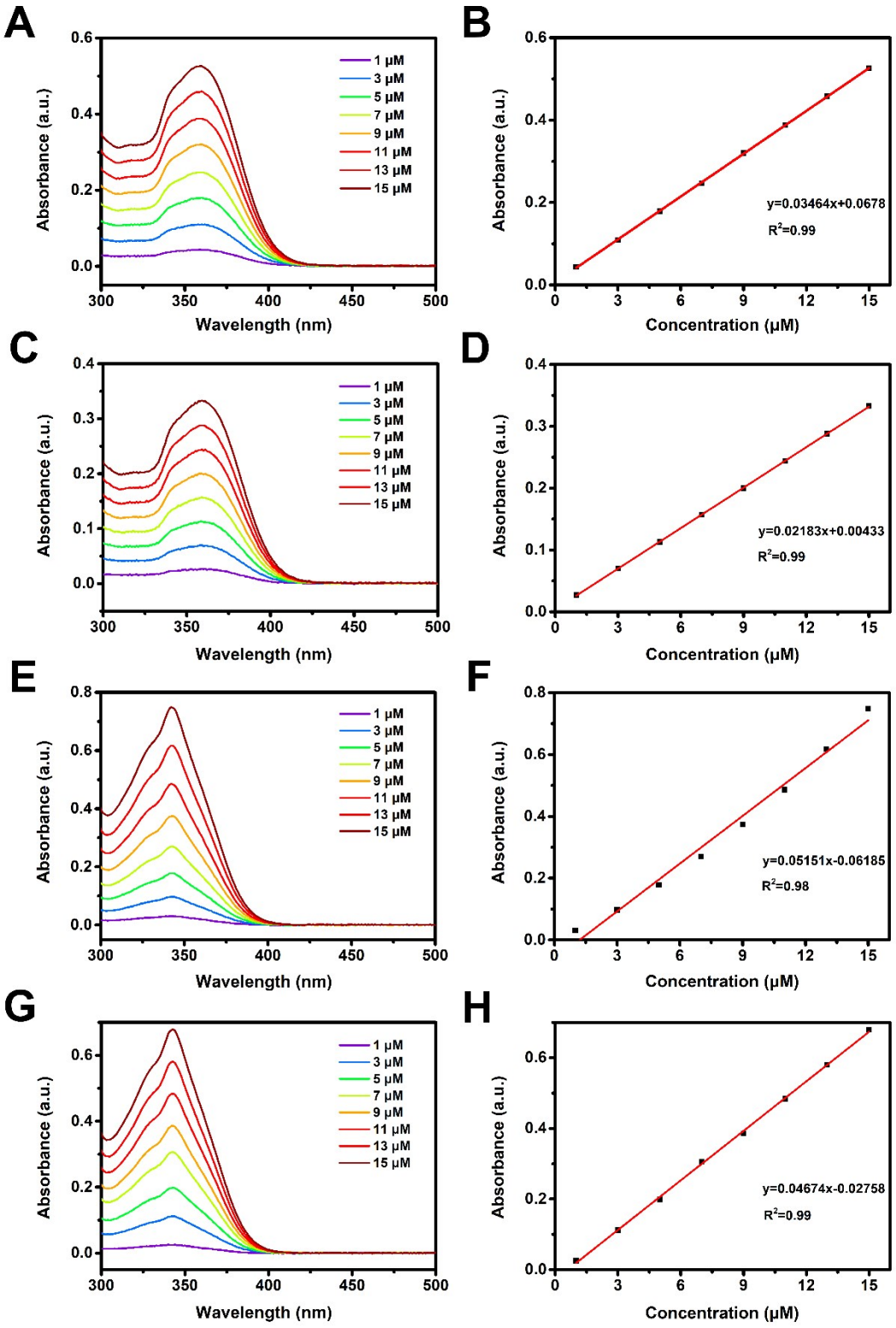


Fig. S1. UV spectra of compound **CPPC** (A), **CHPC** (C), **CPP** (E), **CHP** (G) at different concentrations (1, 3, 5, 7, 9, 11, 13, 15 μM); Absorption-concentration curve of compound **CPPC**(B), **CHPC** (D), **CPP**(F), **CHP**(H).

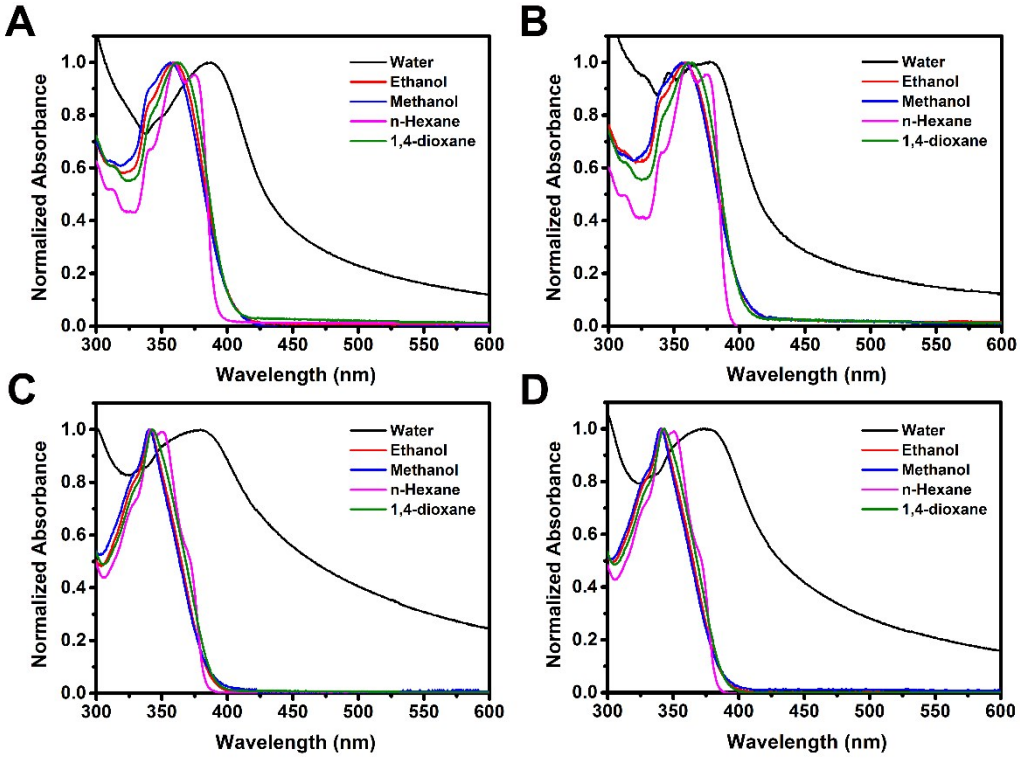
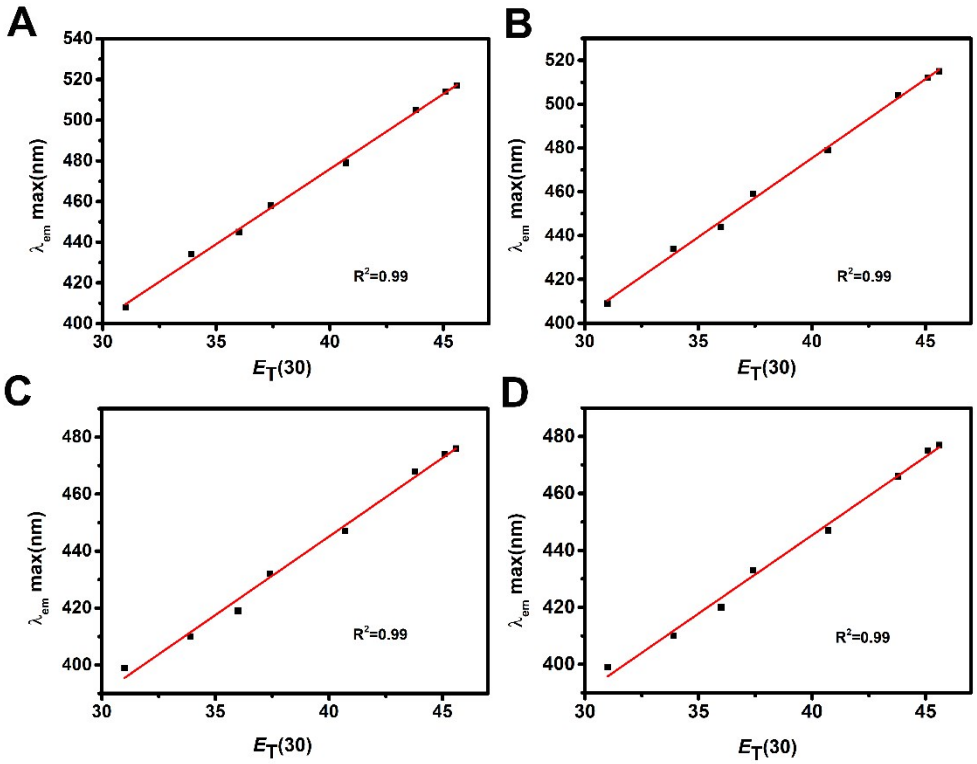


Fig. S2. Absorption spectra of **CPPC**(A), **CHPC**(B), **CPP**(C), **CHP**(D) in different



solvents.

Fig. S3. Linear relationship between the maximum emission wavelength and the

solvent's polarity **CPPC**(A), **CHPC**(B), **CPP**(C), **CHP**(D).

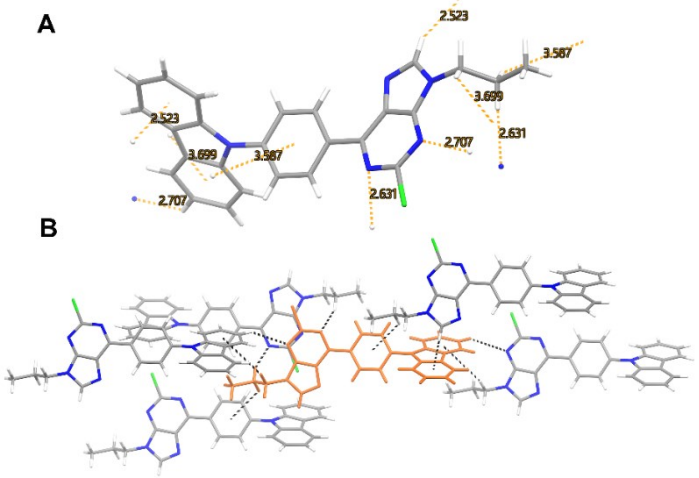


Fig. S4. The detailed intermolecular interactions in **CPPC** crystal.

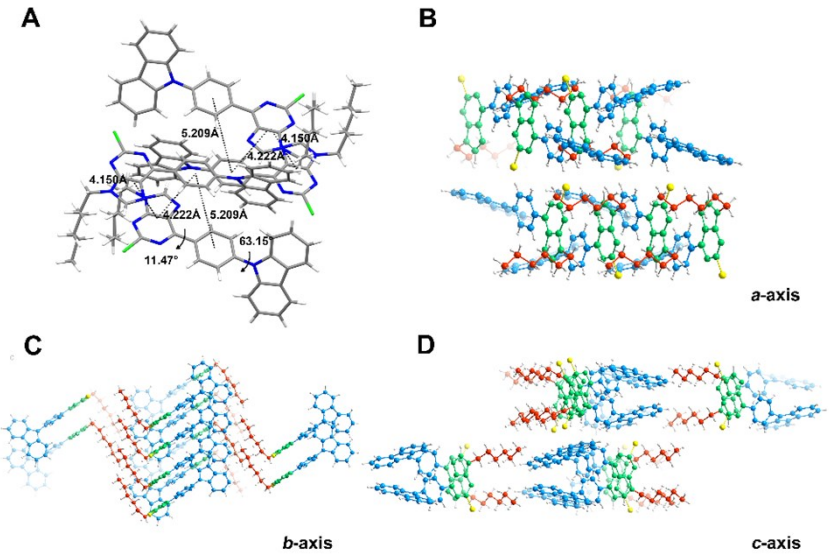


Fig. S5. Single-crystal structure (A) and molecular stacking in **CHPC** single crystal in different views: (B) *a*-axis, (C) *c*-axis, and (D) *b*-axis. The blue parts are carbazole groups, the red parts are alkyl chains, and green parts are purine unit.

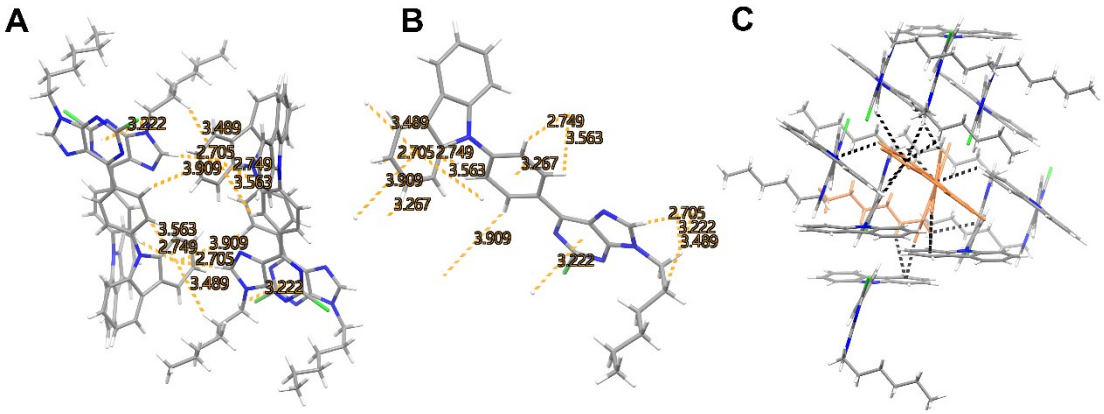


Fig. S6. The detailed intermolecular interactions in **CHPC** crystal.

Table S1. The intermolecular hydrogen bonds data in entire packing modes of the **CPPC** crystal.

Type of interaction	Amount	d/Å
C-H…π	2	2.523
	2	3.587
	2	3.699
C-H…N	2	2.631
	2	2.707

Table S2. The intermolecular hydrogen bonds data in entire packing modes of the **CHPC** crystal.

Type of interaction	Amount	d/Å
C-H…π	2	2.705
	2	2.749
	2	3.222
	2	3.267
	2	3.489
	2	3.563
	2	3.909

Table S3 Crystal data and structure refinement of **CPPC** and **CHPC**.

Compound	**CPPC**	**CHPC**
Formula	$C_{26}H_{20}ClN_5$	$C_{29}H_{26}ClN_5$
$D_{calc.}$/ g cm^{-3}	1.395	1.290
μ/mm^{-1}	1.814	1.574
Size/mm^3	0.20×0.15×0.10	0.15×0.2×0.2
T/*K*	150	150
Crystal System	triclinic	monoclinic
Space Group	***P***-1	P 1 21/c 1
a/Å	8.9375(3)	17.2831(14)

b/Å	10.2919(3)	17.2445(12)
c/Å	11.4557(4)	8.2948(7)
α/°	89.084(2)	90
β/°	88.820(2)	90.889(6)
γ/°	81.768(2)	90
V/Å^3	1042.57(6)	2471.9(3)
F(000)	456.0	1008.0
Z	2	4
Measured Refl's.	20436	25763
Indep't Refl's	4238	4862
R_{int}	0.0554	0.1616
Parameters	290	317
Restraints	0	0
GooF	1.038	1.020
Final R indexes [I>=2σ (I)]wR2 *(all data)*	R_1 = 0.0400, wR_2 =0.0934	R_1 = 0.1128, wR_2 = 0.2836
Final R indexes [all data]	R_1 = 0.0534, wR_2 = 0.1014	R_1 = 0.1540, wR_2 = 0.3488
CCDC	2026792	2015608

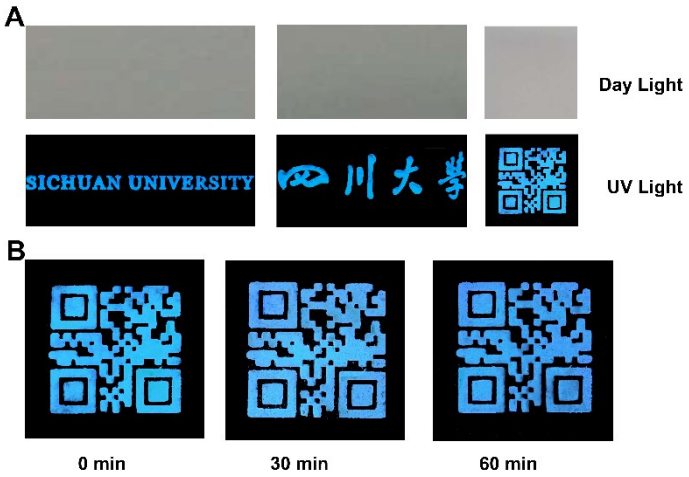


Fig. S7. Anti-counterfeiting protection applications of the **CHPC** compound-based ink. (A) the stamped bilingual logo of school under 365 nm UV lamp, (B) the tamped QR codes under visible light and UV light (365 nm), and irradiated continuously for different time.

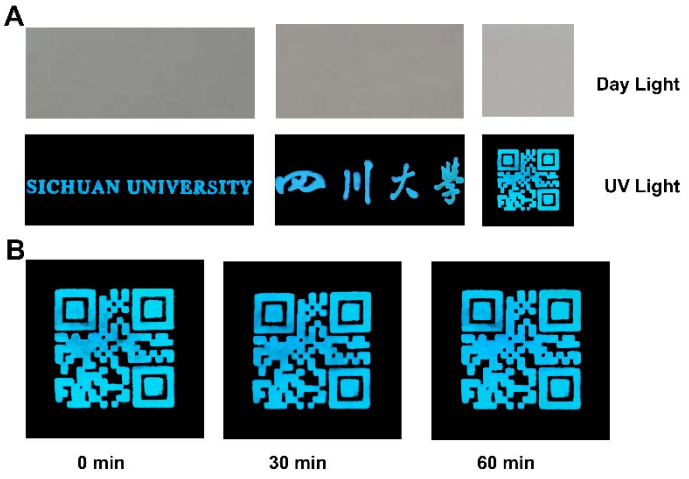


Fig. S8 Anti-counterfeiting protection applications of the **CPP** compound-based ink. (A) the stamped bilingual logo of school under 365 nm UV lamp, (B) the tamped QR codes under visible light and UV light (365 nm), and irradiated continuously for different time.

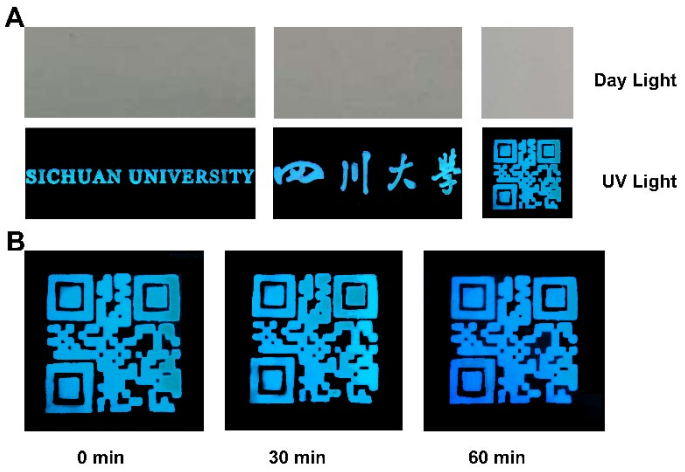


Fig. S9. Anti-counterfeiting protection applications of the **CHP** compound-based ink. (A) the stamped bilingual logo of school under 365 nm UV lamp, (B) the tamped QR codes under visible light and UV light (365 nm), and irradiated continuously for different time.

Table S4 The ClogP values of all compounds.

Compound	**CPPC**	**CHPC**	**CPP**	**CHP**
ClogP	7.38	8.97	12.72	14.31

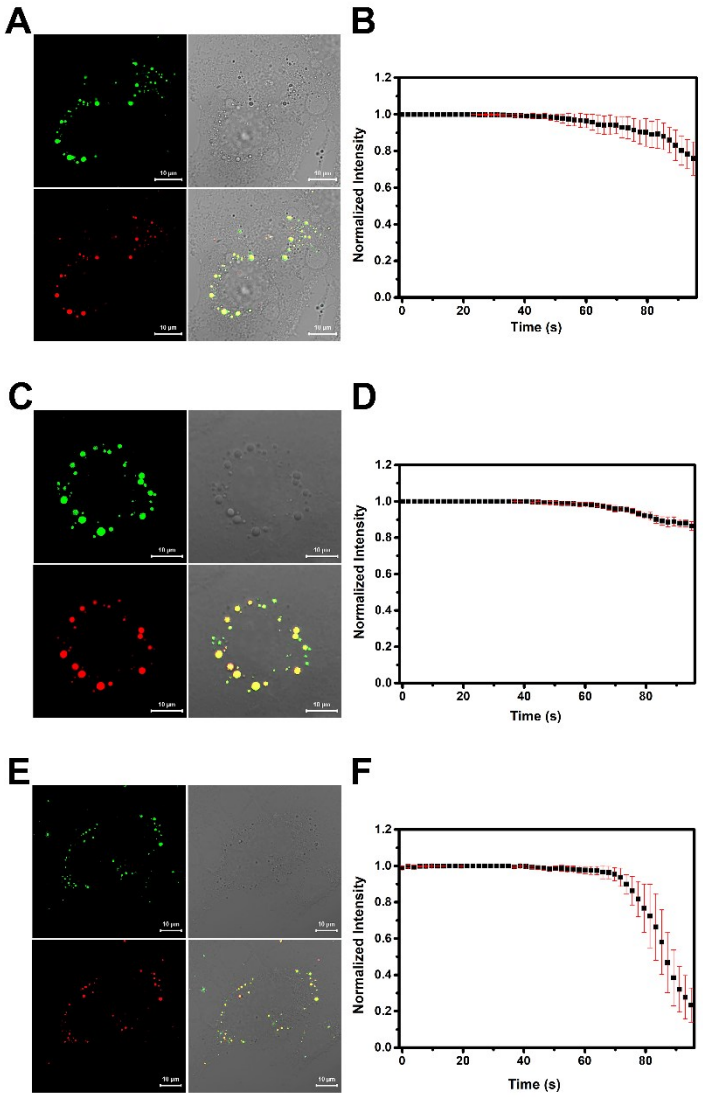


Fig. S10. (A, C, E) CLSM images of HepG2 cells incubated with compounds (**CHPC**, **CPP** and **CHP** respectively)and Nile red, Compound Channel, λ_{ex}=405 nm. Nile red channel, λ_{ex}=543 nm. (B, D, F) Fluorescent signal change of HepG2 cells stained with compounds (**CHPC**, **CPP** and **CHP** respectively) under continuous laser irradiation

NMR DATA

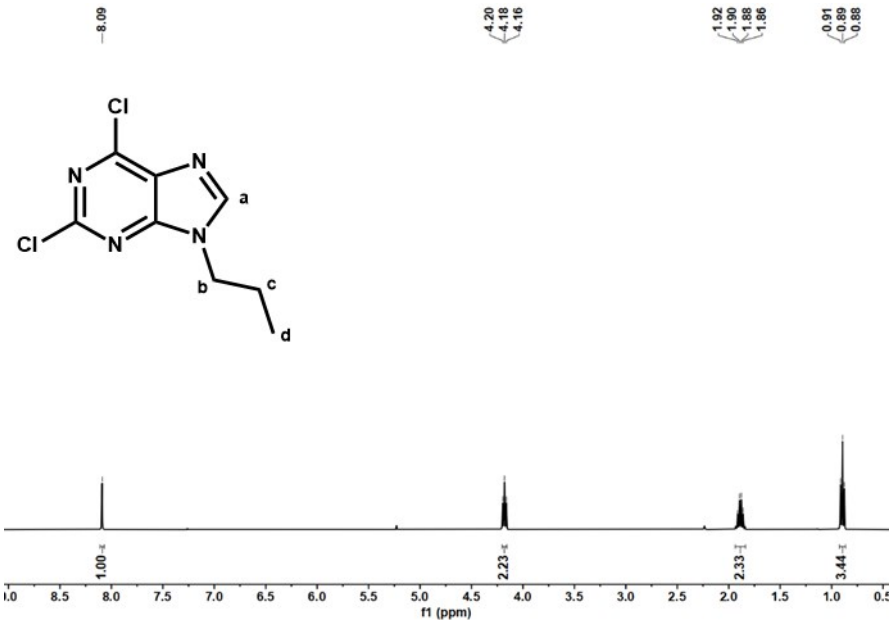


Fig. S11 ^{1}H NMR of Compound **2** in $CDCl_3$

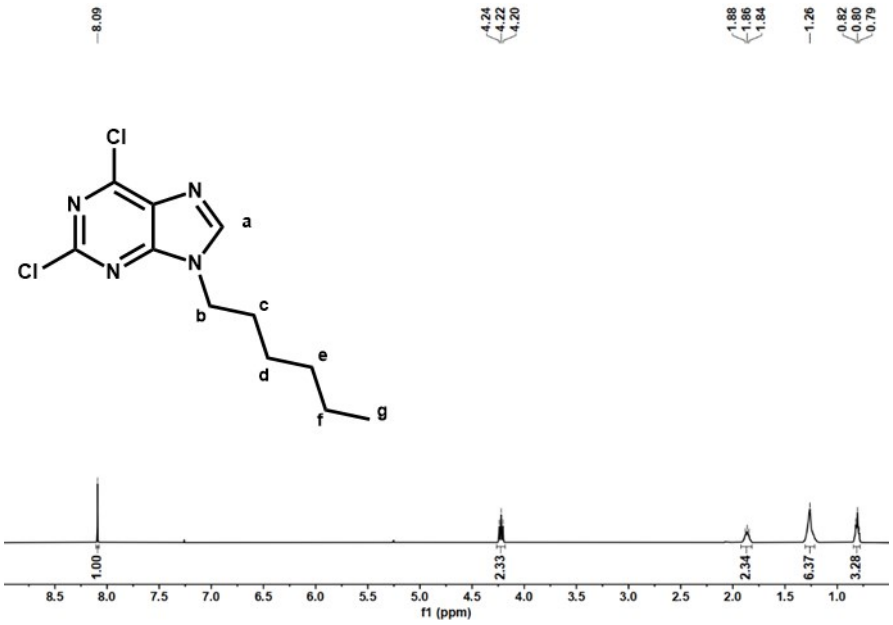


Fig. S12 ^{1}H NMR of Compound **3** in $CDCl_3$

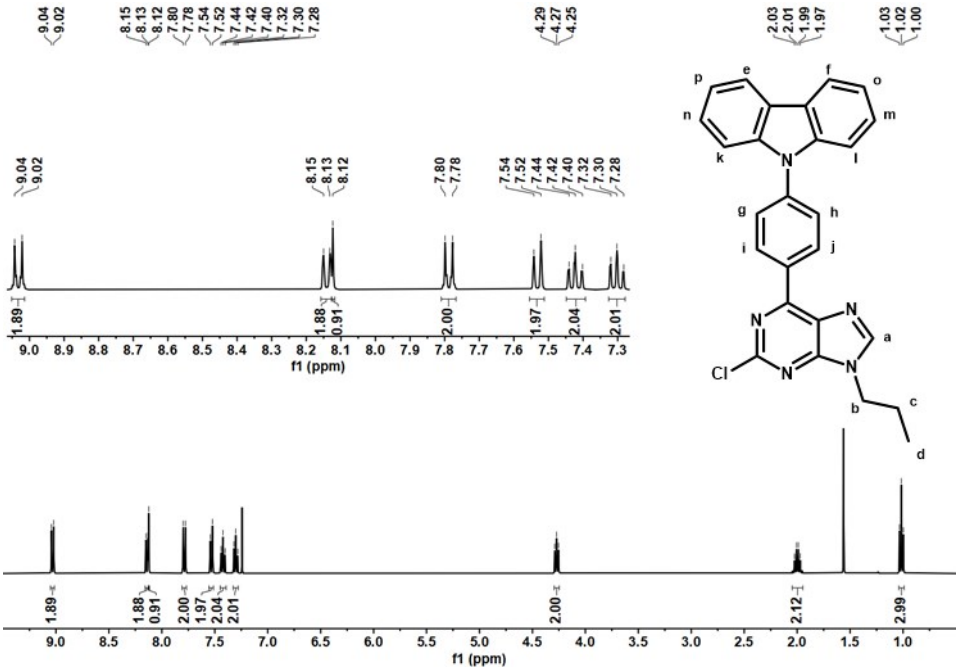


Fig. S13 ^{1}H NMR of Compound **CPPC** in $CDCl_3$

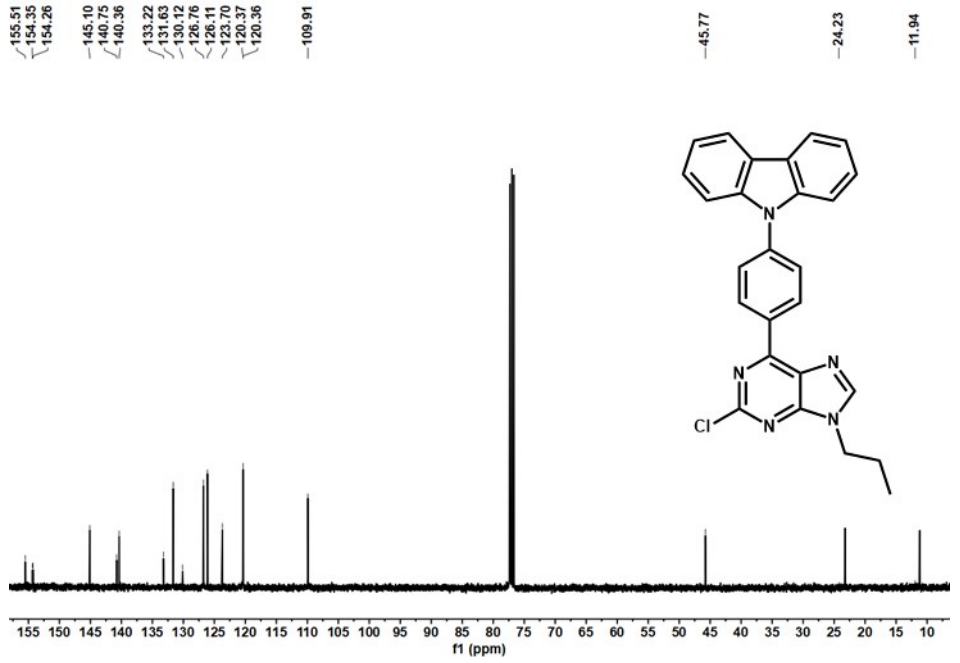


Fig. S14^{13}C NMR of Compound **CPPC** in $CDCl_3$

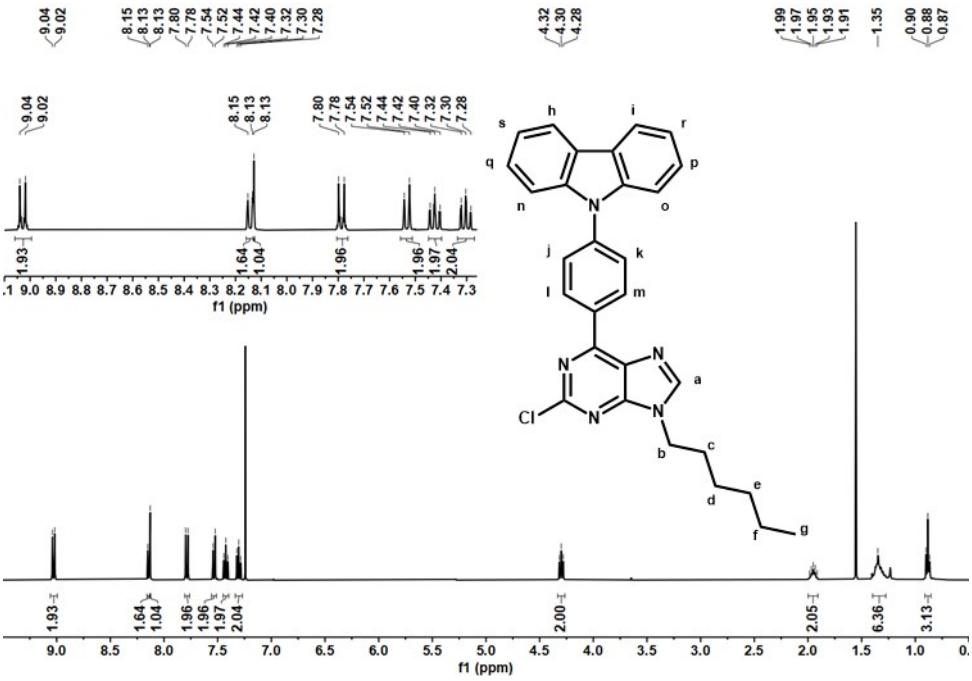


Fig. S15 ^{1}H NMR of Compound **CHPC** in $CDCl_3$

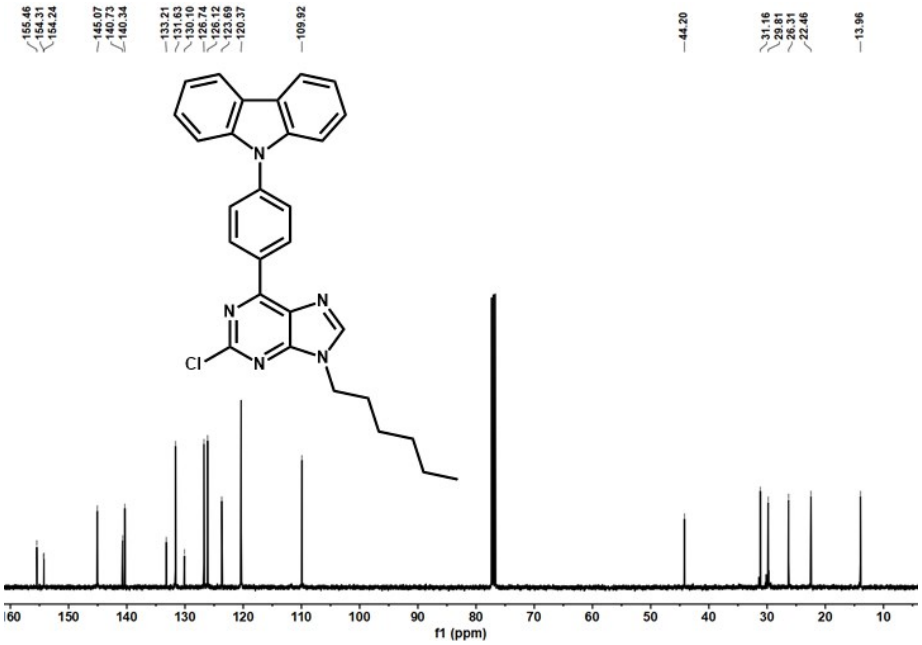


Fig. S16 ^{13}C NMR of Compound **CHPC** in $CDCl_3$

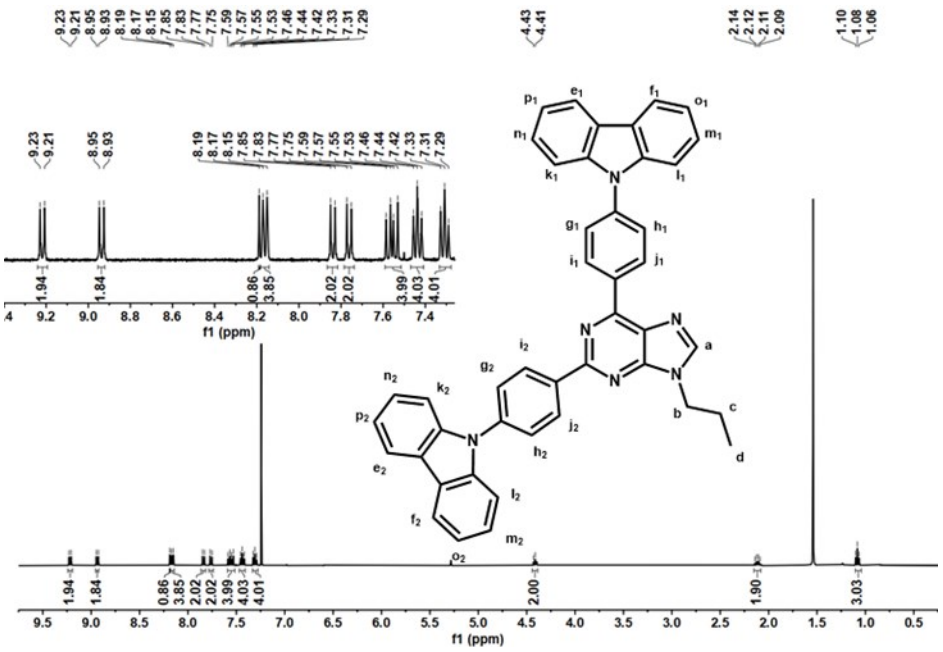


Fig. S17 ^{1}H NMR of Compound **CPP** in $CDCl_3$

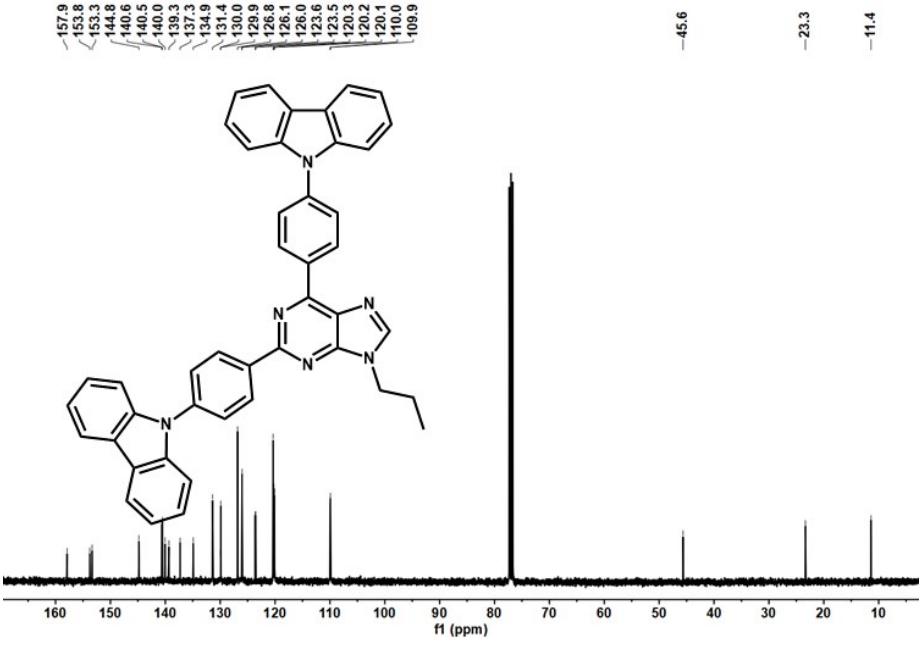


Fig. S18 ^{13}C NMR of Compound **CPP** in $CDCl_3$

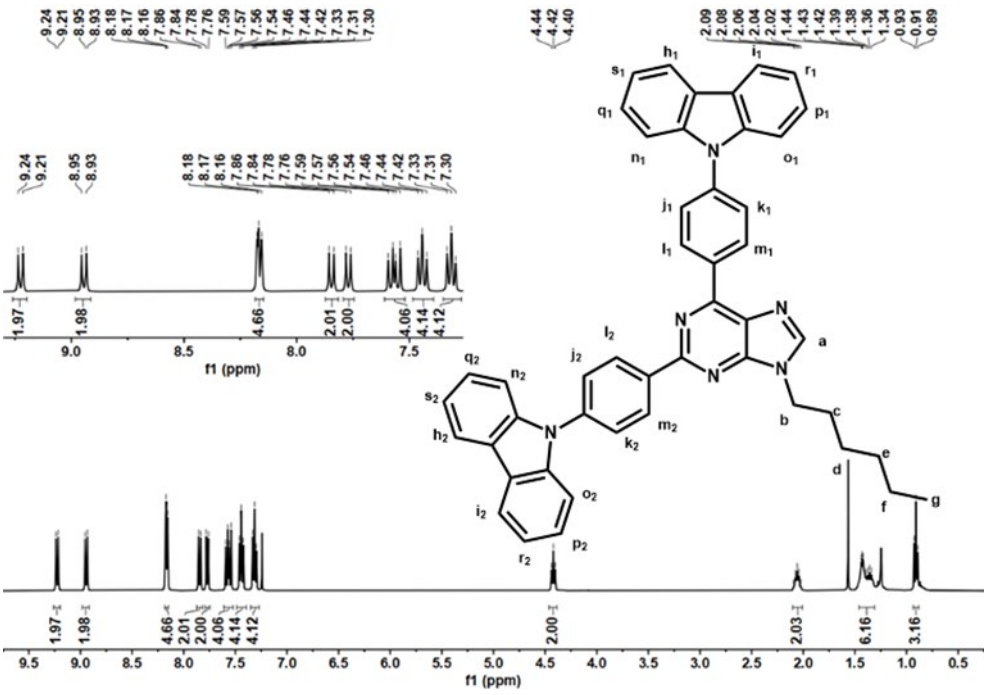


Fig. S19 ^{1}H NMR of Compound **CHP** in $CDCl_3$

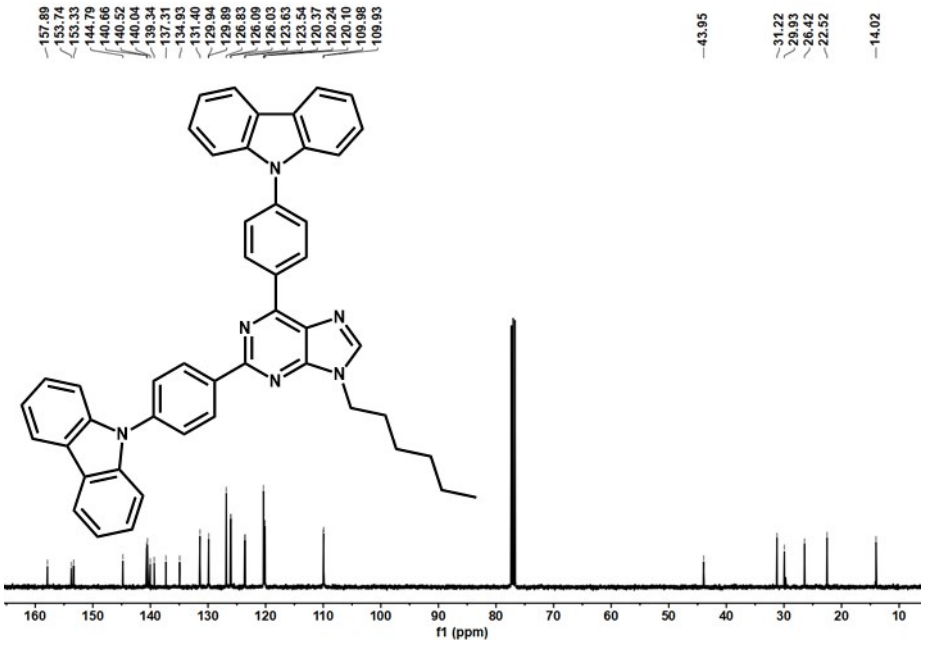


Fig. S20 ^{13}C NMR of Compound **CHP** in $CDCl_3$

ESI-MS Data

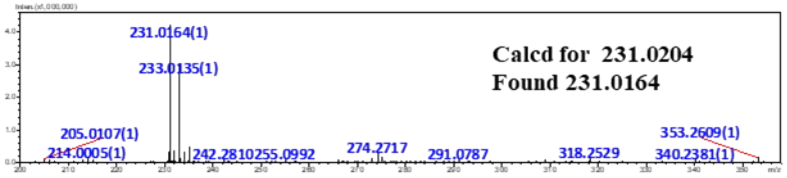


Fig. S21 ESI-MS of Compound **2**

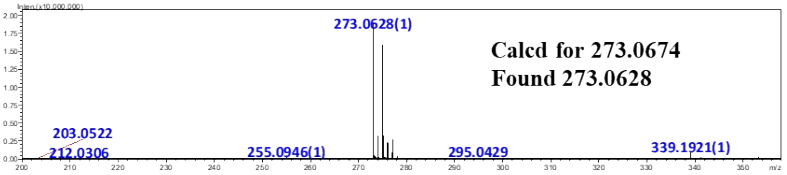


Fig. S22 ESI-MS of Compound **3**

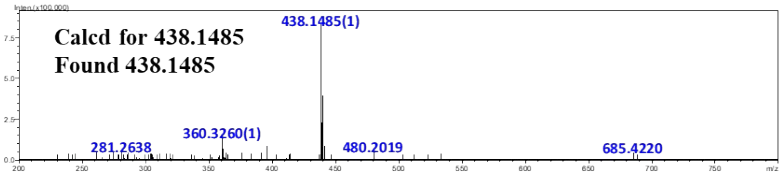


Fig. S23 ESI-MS of Compound **CPPC**.

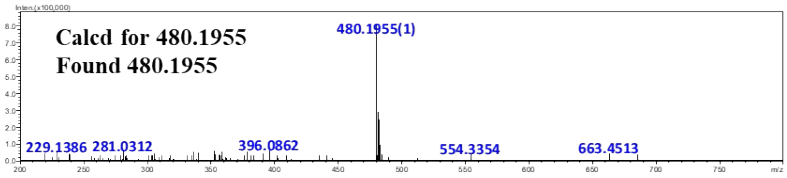


Fig. S24 ESI-MS of Compound **CHPC**.

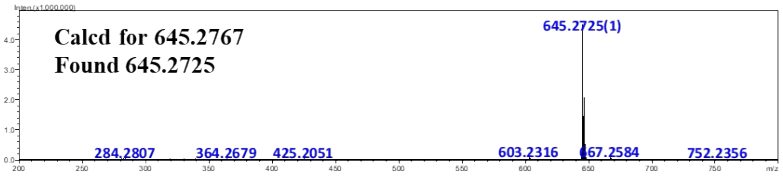


Fig. S24 ESI-MS of Compound **CPP**.

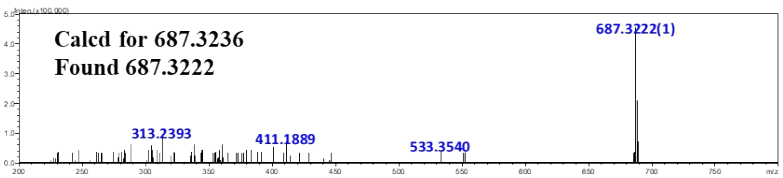


Fig. S25 ESI-MS of Compound **CHP**.

References

1. L. Shi, K. Li, L. L. Li, S. Y. Chen, M. Y. Li, Q. Zhou, N. Wang and X. Q. Yu, *Chem. Sci.*, 2018, **9**, 8969-8974.

2. S.M., Bonesi, M.A., Ponce, and R., Erra-Balsells, *J. Heterocycl. Chem.,* 2004, **41**, 161-171.