Supplementary Material

Multifunctional lipophilic purines: a coping strategy for anti-counterfeiting, lipid droplets imaging and latent fingerprints development

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Experimental section

Apparatus and Measurements

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AM400 NMR spectrometer. ESI-HRMS spectral data were recorded on a Finnigan LCQDECA mass spectrometer. Fluorescence emission spectra came from Hitachi F-7000 spectrometer. Absorption spectra were recorded on a Persee TU-1901 UV-vis Spectrophotometer. The absolute fluorescence quantum yield was measured using a Horiba Fluorolog-3 fluorescence spectrometer with a calibrated integrating sphere system. Single crystal X-ray diffraction intensity data were collected on Bruker APEX-II CCD diffractometer. The ground-state geometries were optimized using the density function theory (DFT) method with B3LYP hybrid functional at the basis set level of 6-31G (d, p). All the calculations were performed using Gaussian 09 package. Confocal lasing scanning microscopic (CLSM) images of came from LSM 780 (Zeiss). The images of developed LFPs were acquired by a JSZ8 microscope (Nanjing Jiangnan NOVEL Optical Co., Ltd.) with a 365 nm illumination and enlarged images of developed LFPs were acquired by an inverted microscope (Nikon Eclipse TS100).

Materials and reagents

All reagents were used without further purification. 2,6-dichloropurine, (4-(9H-carbazol-9-yl)phenyl)boronic acid, 1-bromododecane and iodomethane were obtained from Beijing InnoChem Science & Technology Co.Ltd and Shanghai Aladdin Biochemical Technology Co.Ltd. HepG2 cells were purchased from Shanghai Institute of Biochemistry and Cell Biochemistry and Cell Biology, Chinese Academy of Science. Nile Red were obtained from Thermo Fisher Scientific Inc.

Synthetic procedure

Synthesis of DP

2,6-dichloropurine (2.0 mmol) was dispersed in DMSO (10 mL), and potassium carbonate (3.0 mmol) was added. 1-bromododecane (6.0 mmol) was injected when the mixture was heated up to 50 ℃, and it was stirred for 6 h. After the reaction was completed, water was added and the mixture was extracted with ethyl acetate. At last, white solid was obtained by chromatography on silica gel using ethyl acetate / petroleum ether (1:2) in 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) 8.09 (s, 1H), 4.25 (t, J = 7.3 Hz, 2H), 1.90 (t, J = 6.9 Hz, 2H), 1.32-1.23 (m, 18H), 0.88-0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.13, 152.86, 151.70, 145.70, 130.71, 44.66, 32.33, 31.86, 29.75, 29.54, 29.44, 29.33, 29.29, 28.91, 26.53, 22.65, 14.10. HRMS

(ESI): m/z: Calcd for $C_{17}H_{27}Cl_2N_4^+$: 357.1613 $[M+H]^+$; Found: 357.1610.

Synthesis of CDP

Compound DP (1.25 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (2.75 mmol), potassium carbonate(3.75 mmol) and $Pd(PPh_3)_4$ (0.12 mmol) were poured into a flask, and oxygen was removed from the flask. Deoxygenated 1,4-dioxane (15 mL) and water (3 mL) were injected, and the mixture was stirred at 80 ℃ for 6 h in N_2 atmosphere. When the flask was cooled down, water was added and the mixture was extracted with dichloromethane. CDP was purified by column chromatography on silica gel with dichloromethane / petroleum ether (1:4) as eluent as a white solid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) δ 9.23 (d, *J* = 8.4 Hz, 2H), 8.96 (d, *J* = 8.6 Hz, 2H), 8.20 (s, 1H), 8.19-8.17 (m, 4H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.61-7.55 (m, 4H), 7.48-7.44 (m, 4H), 7.35-7.31 (m, 4H), 4.45 (t, *J* = 7.1 Hz, 2H), 2.10-2.06 (m, 2H), 1.44 (s, 4H), 1.24 (s, 14H), 0.87-0.83 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.88, 153.74, 153.33, 144.77, 140.64, 140.51, 140.03, 139.33, 137.30, 134.92, 131.38, 129.93, 129.87, 126.82, 126.06, 126.00, 123.62, 123.53, 120.35, 120.21, 120.08, 109.96, 109.90, 43.95, 31.87, 29.95, 29.61, 29.59, 29.54, 29.46, 29.31, 29.04, 26.73, 22.65, 14.09. HRMS (ESI): m/z: Calcd for $C_{53}H_{51}N_6^+$: 771.4175; $[M+H]^+$ Found: 771.4189.

Synthesis of CDPI

Compound CDP (0.05 mmol) was added into a Pressure Vessel. Whereafter, acetonitrile (1 mL) and iodomethane (0.5 mL) were injected and stirred at 80 ℃ overnight. After the reaction was completed and cooled, the crude product was purified by recrystallization and silica gel column chromatography with dichloromethane / methanol (50:1) as eluent. Finally, CDPNI was obtained as yellow solid in 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (TMS, ppm) δ 11.39 (s, 1H), 8.86 (d, *J* = 8.5 Hz, 2H), 8.17-8.15 (m, 4H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.57-7.53 (m, 4H), 7.48-7.41 (m, 4H), 7.36-7.30 (m, 4H), 4.80 (t, *J* = 7.6 Hz, 2H), 4.32 (s, 3H), 2.33-2.29 (m, 2H), 1.48 (s, 2H), 1.21 (s, 16H), 0.84-0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.68, 155.54, 150.81, 146.11, 141.32, 141.29, 140.28, 140.09, 134.15, 132.11, 131.49, 130.65, 127.08, 126.89, 126.33, 126.15, 123.92, 123.77, 120.84, 120.57, 120.49, 120.46, 120.34, 109.81, 109.63, 46.67, 38.75, 31.86, 29.64, 29.61, 29.59, 29.47, 29.31, 29.00, 26.69, 22.64, 14.08. HRMS (ESI): m/z: Calcd for $C_{54}H_{53}N_6^+$: 785.4326; $[M-I]^+$ Found: 785.4350.

Cell culture

HepG2 cells were cultured in Dulbecco's modified Eagle medium (DMEM) supplemented with 10% fetal bovine serum and 1% antibiotic-antimycotic at 37℃ in a 5% CO_2 / 95% air incubator.

Cell imaging

HepG2 cells were incubated confocal plates for 12 h. Culture mediums containing different dye (containing 0.1 vol% stock solution of dye, 9.9 vol% DMSO, 40 vol% PEG-400 and 50 vol% DMEM,) were prepared. HepG2 cells were stained with culture medium at 37 ℃ for 30 min and washed two or three times with PBS. Afterwards, HepG2 cells were stained with Nile Red at 37 ℃ for 15 min and washed two or three times with PBS. The cells were imaged with proper conditions for each dye: **CDP** (λ_{em}= 400-500 nm) and **CDPI** (λ_{em}= 430-550 nm) under the excitation of 405 nm, and Nile Red (λ_{em}= 600-700 nm) under the excitation of 543 nm.

Preparation of the anti-counterfeiting ink and LFPs development solution

The anti-counterfeiting ink contained of 80% 1,4-dioxane and 20% glycerol. The LFPs development solution contained 40% 1,4-dioxane, 30% PEG-400 and 30% water.

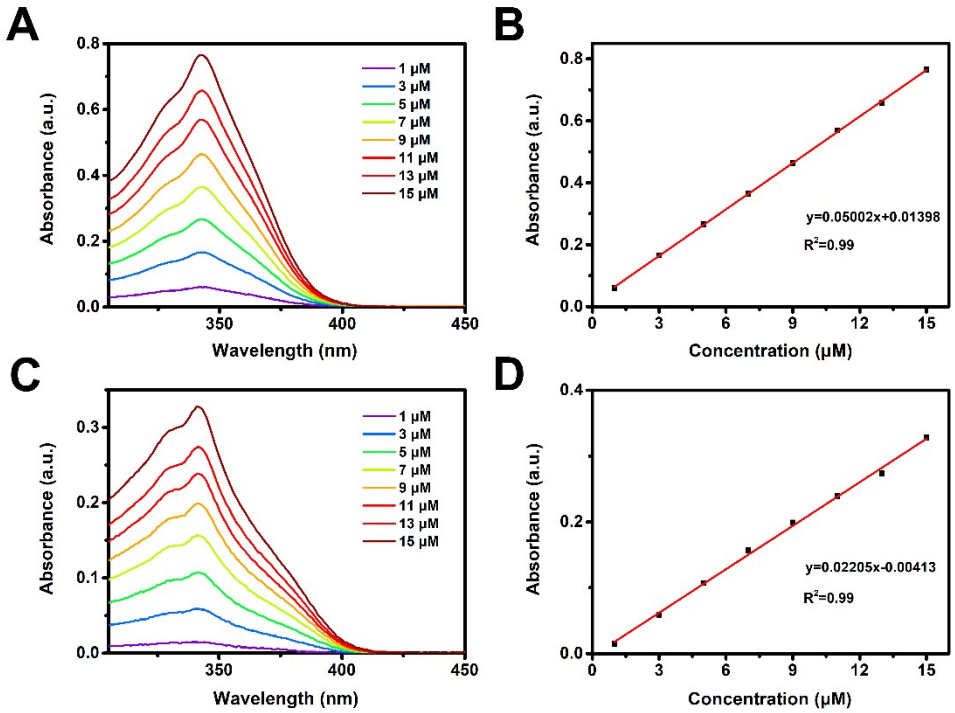


Figure S1. UV spectra of compound **CDP** (A), **CDPI** (C) at different concentrations (1, 3, 5, 7, 9, 11, 13, 15 μM); Absorption-concentration curve of compound **CDP** (B), **CDPI** (D).

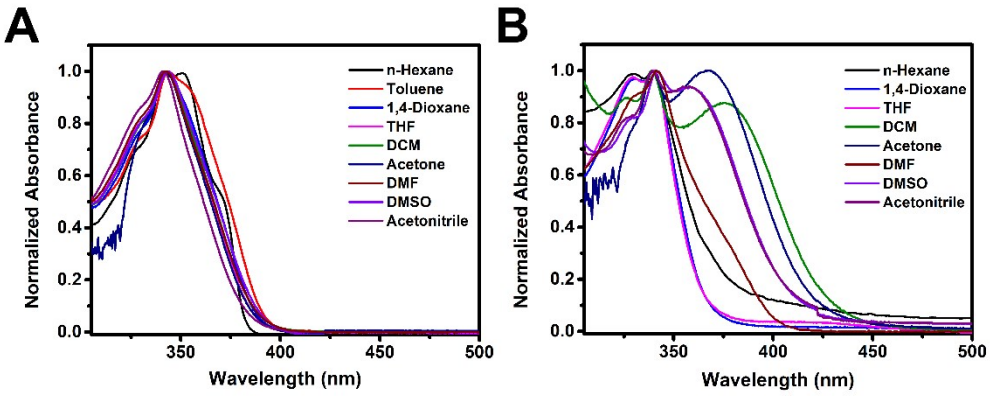


Figure S2. Absorption spectra of **CDP** (A) and **CDPI** (B) in different solvents.

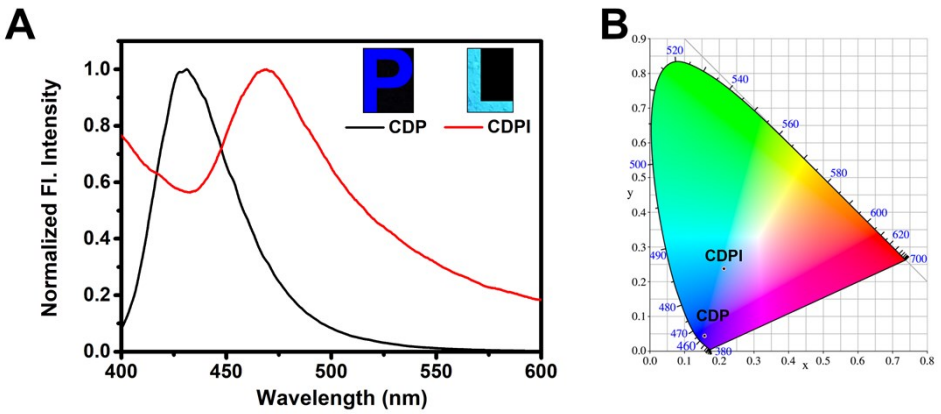


Figure S3. (A) Solid fluorescence spectra of **CDP** and **CDPI**, inset: photographs of the fluorescence of **CDP** and **CDPI** taken under UV lamp excitation (365 nm); (B) Solid fluorescence spectra of **CDP** and **CDPI** plotted on a CIE 1931 chromaticity diagram.

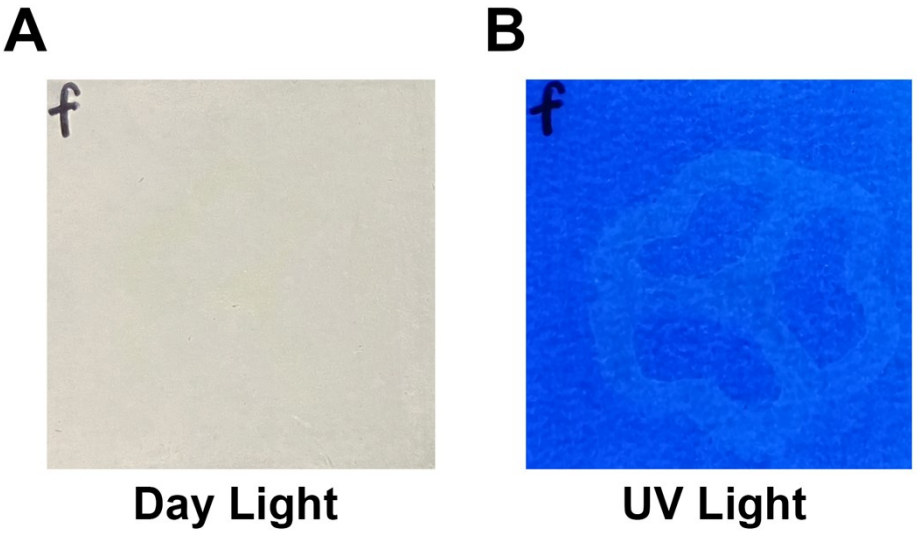
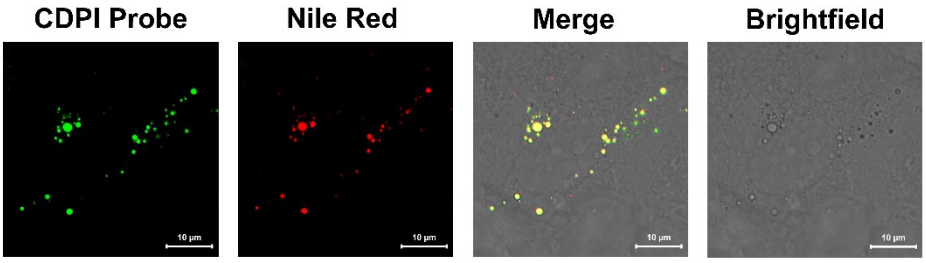


Figure S4. Anti-counterfeiting protection applications of the **CDPI** compound-based ink. Anti-counterfeiting labels based four kinds of patterns the under day light (A) and 365 nm UV lamp (B).



Figue S5. CLSM images of HepG2 cells incubated with compound (**CDPI**) and Nile red: Compound Channel, λ_{ex}=405 nm; Nile red channel, λ_{ex}=543 nm; Merged of compound and Nile red channel, and Brightfield.

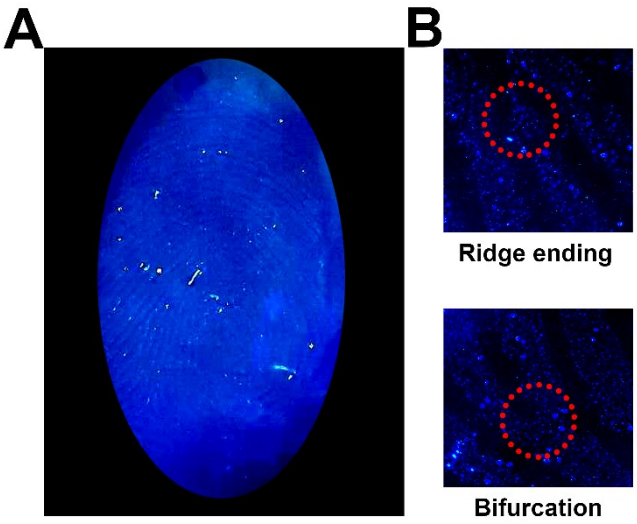


Figure S6. Photographs of latent fingerprints after developing with **CDPI** (A); Enlarged details of the photograph, including ridge ending and bifurcation, core. All photographs were taken under the excitation of UV illumination (365 nm).

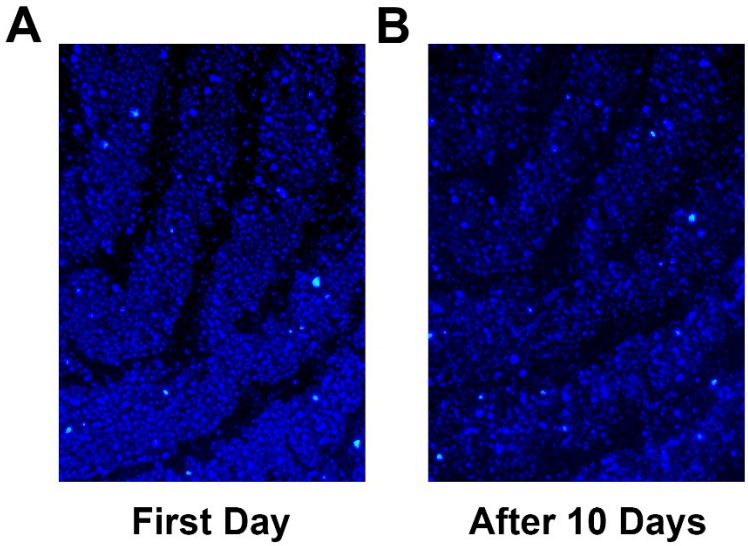


Figure S7. Stability test of fingerprint developing agent (**CDP**): Fluorescent images of developed latent fingerprints on glass was obtained at first day (A), after 10 days (B).

Table S1 Crystal data and structure refinement of **CDP**.

Compound	**CDP**
Formula	$C_{53}H_{50}N_6$
$D_{calc.}$/ g cm^{-3}	1.213
μ/mm^{-1}	0.553
Size/mm^3	0.20×0.15×0.12
T/*K*	152
Crystal System	triclinic
Space Group	$P\bar{1}$
a/Å	9.1867(2)
b/Å	15.7160(4)
c/Å	16.2136(4)
α/°	66.9530(10)
β/°	83.8400(10)
γ/°	78.7110(10)
V/Å^3	2111.15(9)
F(000)	820.0
Z	2
Measured Refl's.	77546
Indep't Refl's	9015
R_{int}	0.0461
Parameters	533

Restraints	0
GooF	1.039
Final R indexes [I>=2σ (I)]wR2	R_1 = 0.0706, wR_2 =0.1848
Final R indexes [all data]	R_1 = 0.0870, wR_2 = 0.1988
CCDC	2014011

NMR DATA

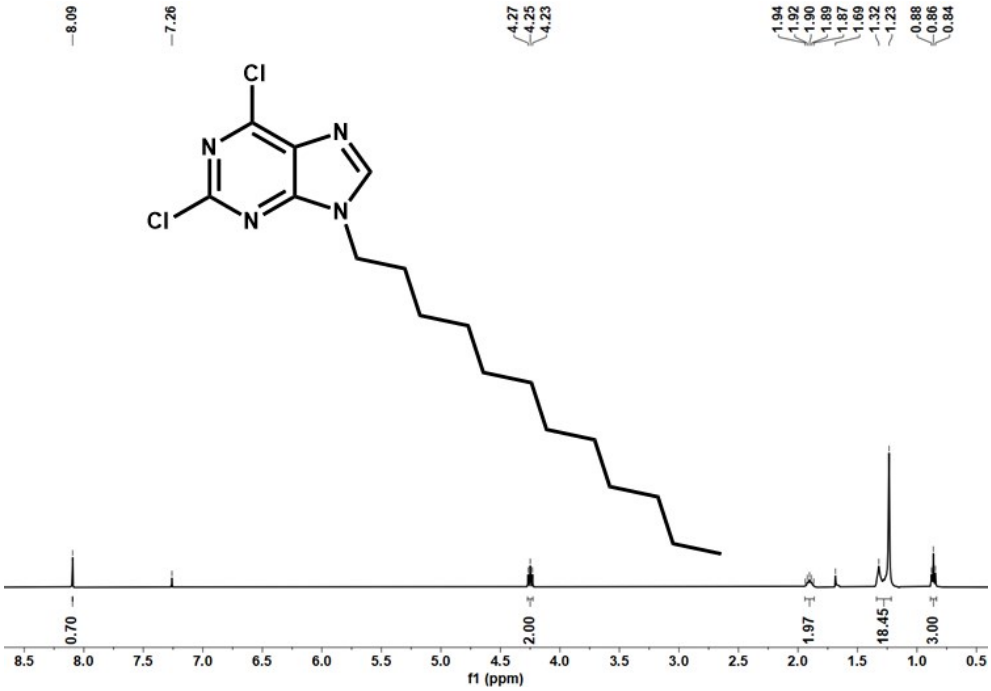


Figure S8. ^{1}H NMR of **DP** in $CDCl_3$.

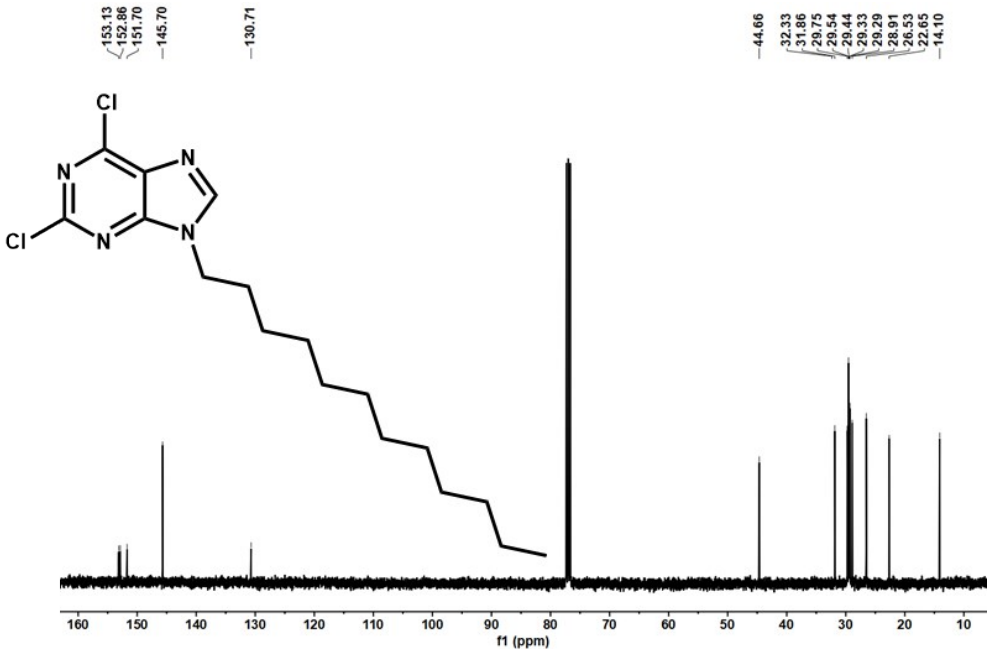


Figure S9. ^{13}C NMR of **DP** in $CDCl_3$.

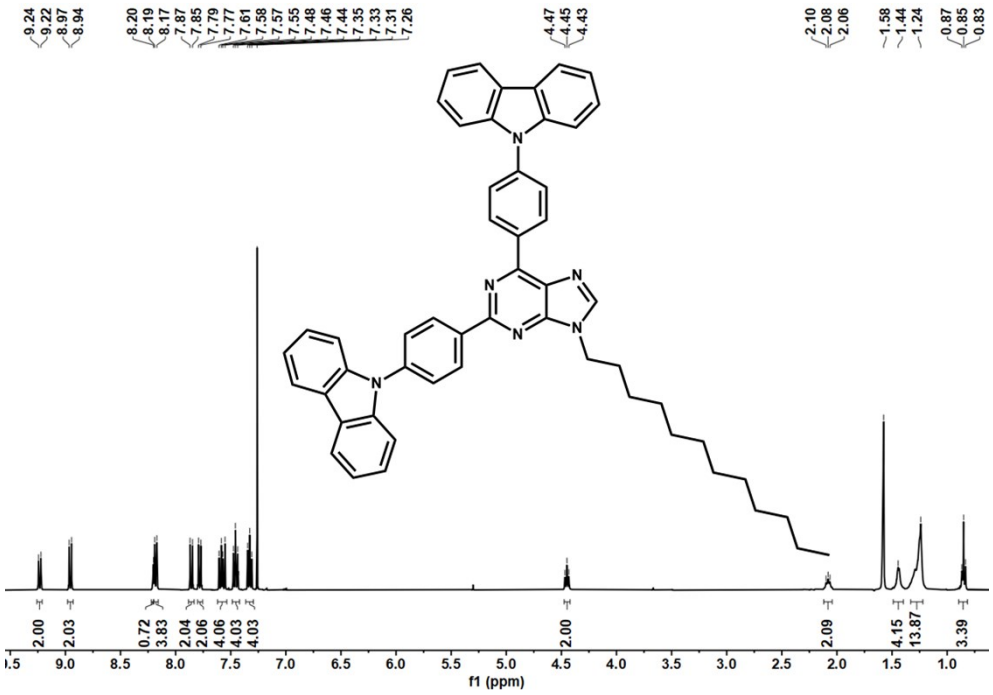


Figure S10. ^{1}H NMR of **CDP** in $CDCl_3$.

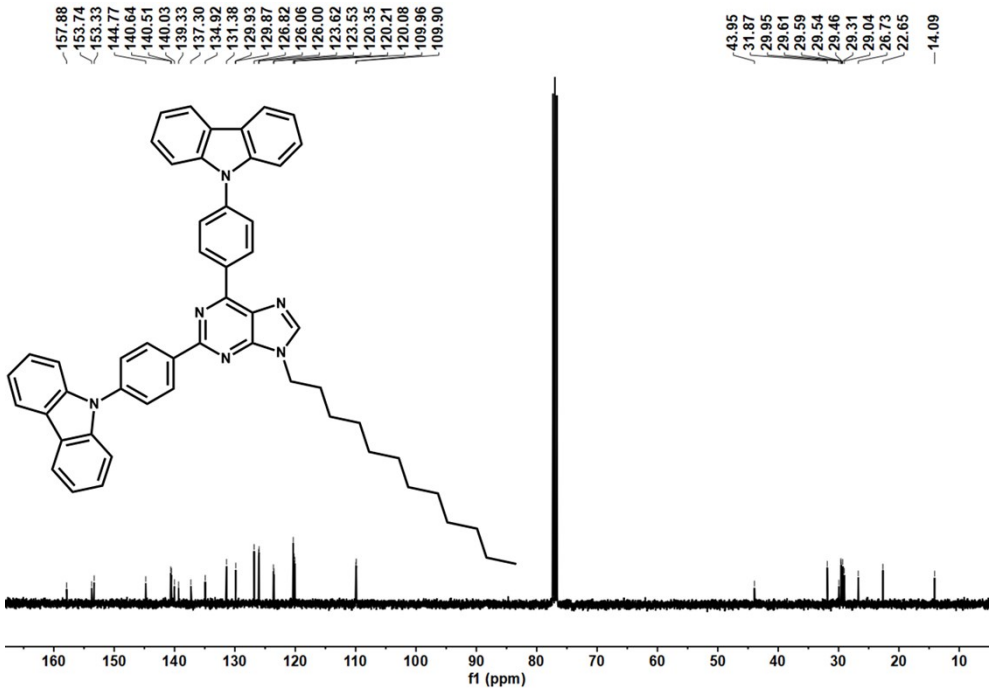


Figure S11. ^{13}C NMR of **CDP** in $CDCl_3$.

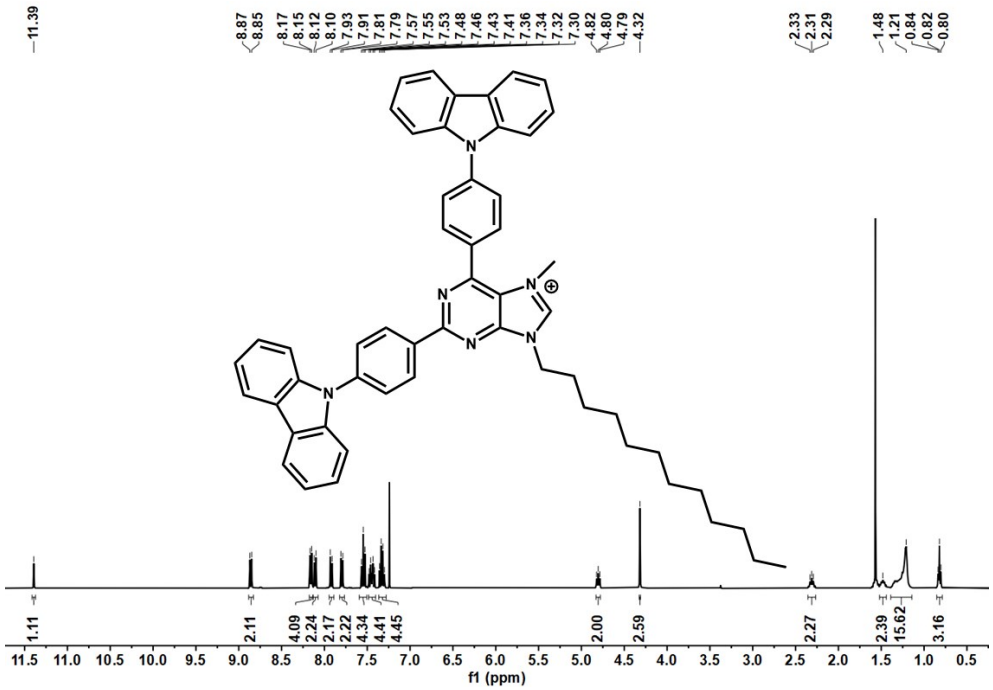


Figure S12. ^{1}H NMR of **CDPI** in $CDCl_3$.

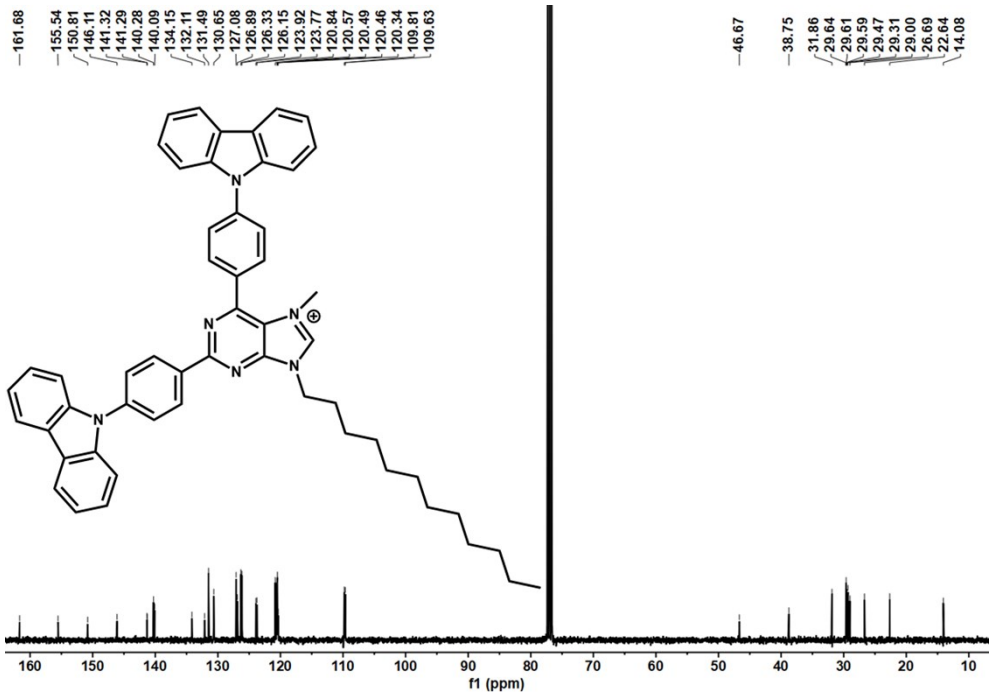


Figure S13 ^{13}C NMR of **CDPI** in $CDCl_3$.

ESI-MS Data

DP

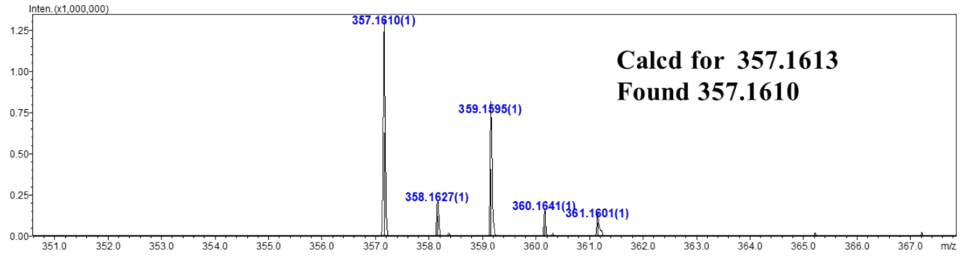


Figure S14. ESI-MS Data of **DP**.

CDP

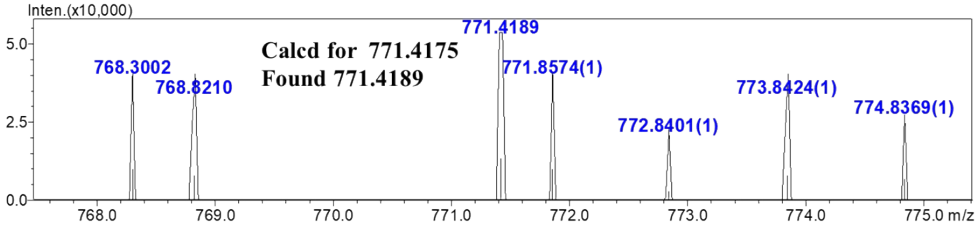


Figure S15. ESI-MS Data of **CDP**.

CDPI

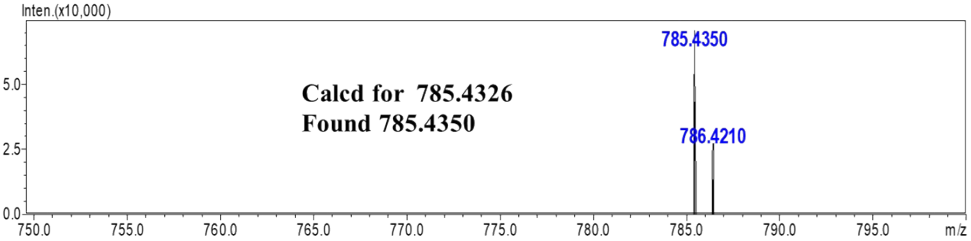


Figure S16. ESI-MS Data of **CDPI**.