Supplementary Information

Regioisomers of carbazole & triphenylamine based D-A-D ternaries: Synthesis, optical properties and colorimetric vapochromic anti-counterfeiting application

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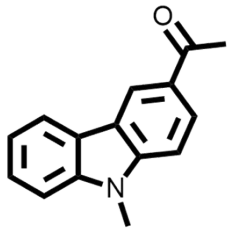
Materials and Methods

Carbazole was purchased from Hi-media (India), Triphenylamine was purchased from Sigma-Aldrich (India), Anhydrous $AlCl_3$ was purchased from Spectrochem (India), Acetyl chloride was purchased from TCI (India), Tertiary Butyl Chloride was purchased from AVRA (India), Anhydrous $ZnCl_2$ was purchased from Merck (India), Deuterated chloroform was purchased from Sigma-Aldrich. All the UV-Vis and fluorescence spectroscopy experiments are conducted by using Analytical grade and freshly distilled solvent at room temperature. Absolute quantum yield was calculated using integrating sphere and Relative quantum yield was calculated using Anthracene as a standard reference. The ^{1}H and ^{13}C NMR experiments are recorded on a Bruker 300 MHz NMR spectrometer in $CDCl_3$, Mass Spectrum was recorded on a Agilent Technologies G6528A UHD High Resolution Mass Spectrometer, Solid state fluorescence, Lifetime, and Relative quantum yield was recorded on a Edinburg instruments FLS 1000 Photoluminescence spectrometer, Liquid state fluorescence was recorded on a JASCO FP-8300 spectrofluorometer, Electronic absorption spectrum was recorded on a JASCO V-730 UV-Vis spectrophotometer, Single Crystal X-ray diffraction studies was carried out on a Bruker D8 Quest Eco spectrometer.

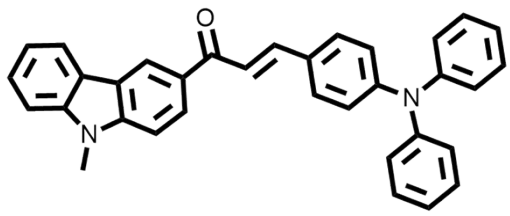
Synthesis of Methyl carbazolyl ketone



5 g (27.6 mmol, 1 equivalent) of 9H 9-methyl Carbazole and 2.38 g of Acetyl chloride (30.36 mmol, 1.1 equivalent) was dissolved in 100 ml of DCM under nitrogen atmosphere. To the mixture 4.51 g of anhydrous $ZnCl_2$ was added over the course of 45 min and heated to 50 ^{o}C for 6 hrs. Completion of the reaction was monitored by TLC and cooled to room temperature, The crude mixture was extracted with Brine/DCM mixture and dried using Na_2SO_4. The crude product was purified as white color solid (4.51g, 73 % yield) by column chromatography using Hexane/Ethyl acetate (90/10 %) and confirmed by ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.20 – 8.10 (m, 2H), 7.59 – 7.48 (m, 1H), 7.48 – 7.36 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 3.89 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$)

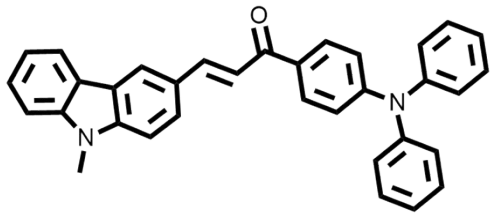
δ 197.72, 143.67, 141.69, 128.82, 126.51, 126.47, 123.09, 122.55, 121.79, 120.55, 120.06, 108.99, 108.06, 77.48, 77.26, 77.06, 76.63, 29.30, 26.66.

Synthesis of 1



250 mg (1.12 mmol, 1 equivalent) of **carbazolyl ketone** and 400 mg (1.45 mmol, 1.3 equivalent) of **triphenylamine aldehyde** was dissolved in 20 ml of ethanol. To that 67 mg (1.68 mmol, 1.5 equivalent) of NaOH was added and stirred for 48 hrs. Formed yellow color precipitate was filtered using Whatman filter paper and washed with cold ethanol, The crude yellow precipitate was extracted with Brine/DCM mixture and dried using anhydrous Na_2SO_4. Analytically pure product (110 mg, 20 %) was obtained by column chromatographic method using Hexane/EA (80/20 %). Crystal was grown by slow diffusion recrystallisation method using Chloroform and Hexane under ambient condition. The product was confirmed by ^1H, ^{13}C NMR, HRMS, Single crystal XRD technique. ^1H NMR (300 MHz, $CDCl_3$) δ 8.83 (d, *J* = 1.6 Hz, 1H), 8.24 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.19 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.85 (d, *J* = 15.5 Hz, 1H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.60 – 7.49 (m, 3H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.44 (t, *J* = 1.0 Hz, 1H), 7.37 – 7.25 (m, 5H), 7.21 – 7.10 (m, 4H), 7.14 – 7.02 (m, 4H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.60, 149.89, 146.99, 143.60, 143.48, 141.72, 130.01, 129.62, 129.50, 128.46, 126.78, 126.46, 125.38, 123.99, 123.17, 122.70, 121.87, 120.66, 120.03, 119.94, 108.97, 108.24, 29.37. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{34}H_{27}N_2O$ = 479.2118; Found = 535.2132.

Synthesis of 2



250 mg (1.11 mmol, 1 equivalent) of **carbazolyl aldehyde** and 446 mg (1.55 mmol, 1.3 equivalent) of **triphenylamine ketone** was dissolved in 20 ml of ethanol. To that 67 mg (1.67 mmol, 1.5 equivalent) of NaOH was added and stirred for 48 hrs. Formed yellow color precipitate was filtered using Whatman filter paper and washed with cold ethanol, The crude yellow precipitate was extracted with Brine/DCM mixture and dried using anhydrous Na_2SO_4. Analytically pure product (80 mg, 15 %) was obtained by column chromatography using Hexane/Ethyl acetate (90/10 %) followed by slow diffusion recrystallisation method with Chloroform and Hexane. The product was confirmed by ^1H, ^{13}C NMR, HRMS, Single crystal XRD technique. ^1H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 1.7 Hz, 1H), 8.13 (dt, *J* = 7.6, 1.0 Hz, 1H), 8.05 (d, *J* = 15.5 Hz, 1H), 7.98 (d, *J* = 8.9 Hz, 2H), 7.79 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.60 (d, *J* = 15.5 Hz, 1H), 7.52 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.38 – 7.28 (m, 5H), 7.22 – 7.11 (m, 6H), 7.08 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.43, 151.86, 146.68, 145.23, 142.33, 141.53, 131.34, 130.07, 129.61, 126.34, 125.91, 124.53, 123.31, 122.73, 121.29, 120.53, 120.14, 119.73, 118.99, 108.87, 29.27. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{34}H_{27}N_2O$ = 479.2118; Found = 479.2143.

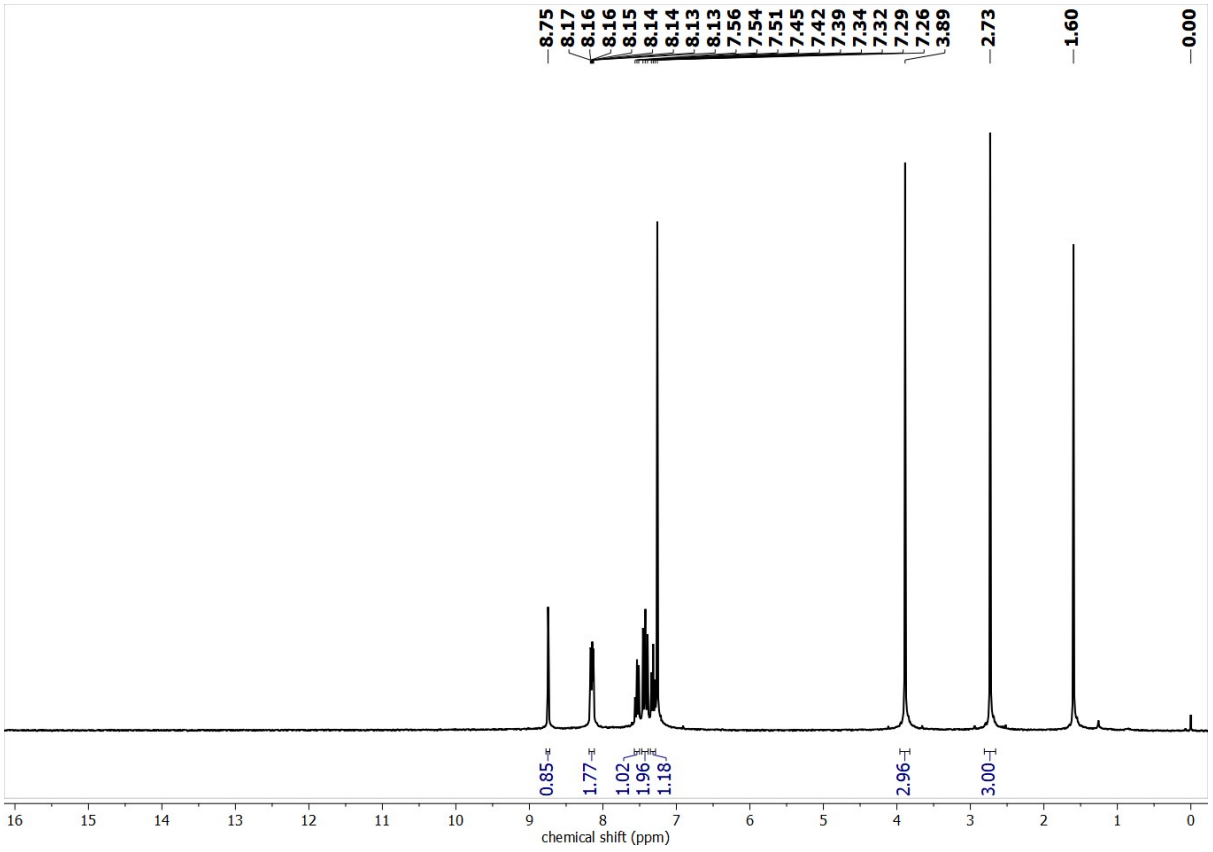


Figure S1: ^{1}H NMR of 3-methyl ketone 9-methyl carbazole in $CDCl_3$

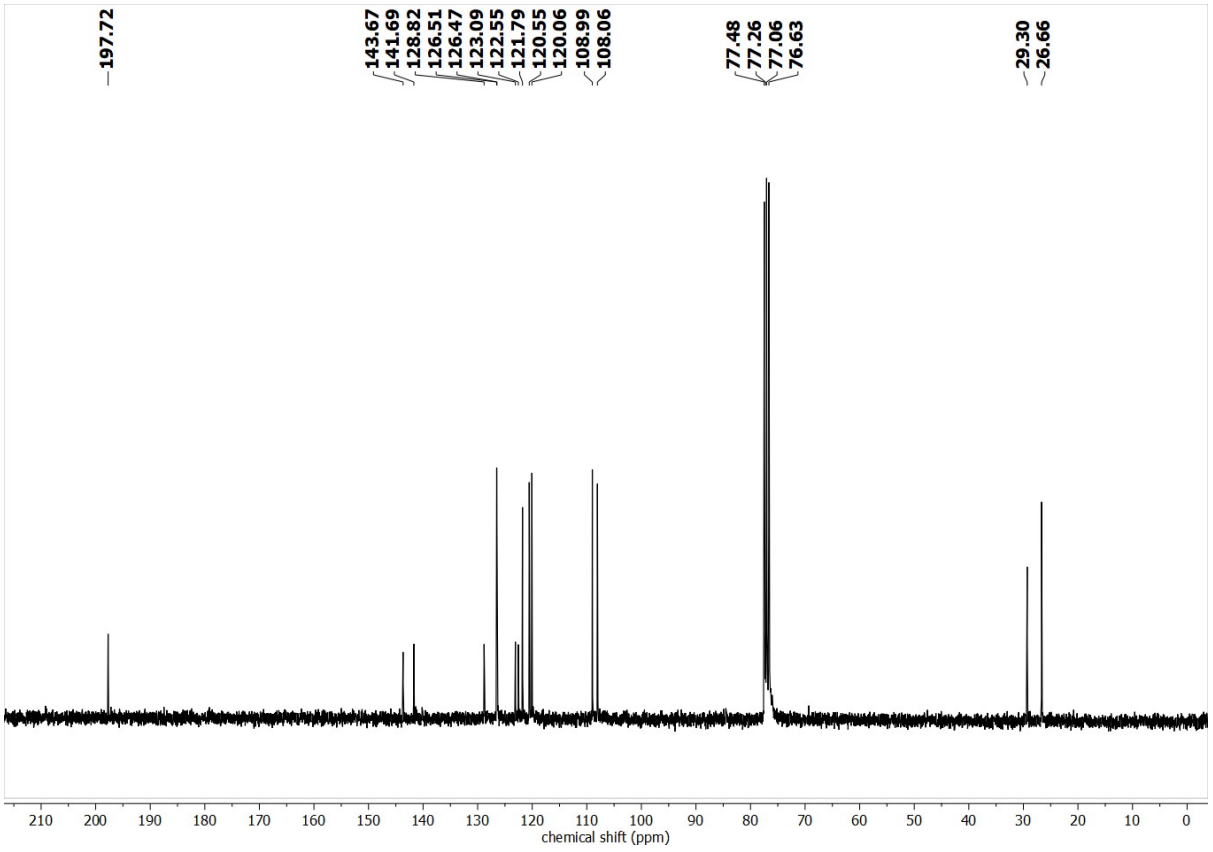


Figure S2: ^{13}C NMR of 3-methyl ketone 9-methyl carbazole in $CDCl_3$

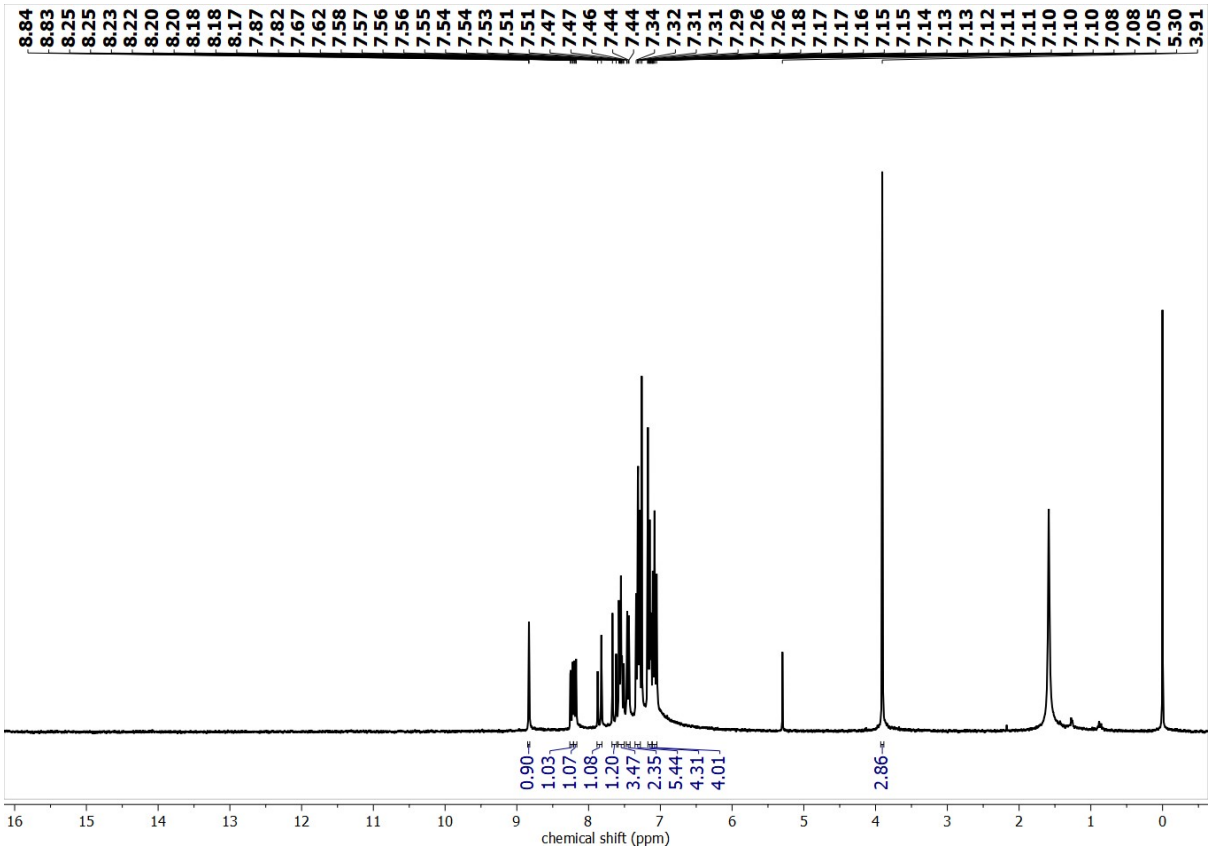


Figure S3: ^{1}H NMR of 1 in $CDCl_3$

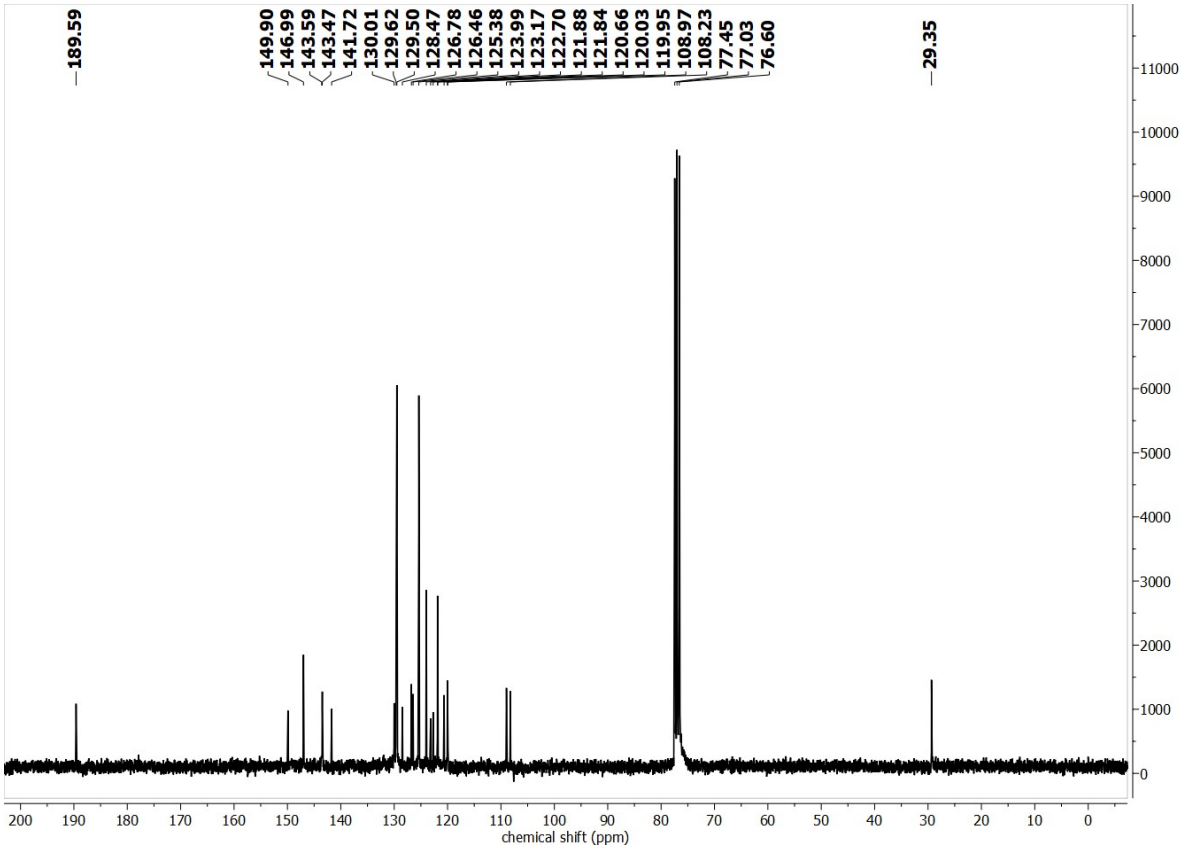


Figure S4: ^{13}C NMR of 1 in $CDCl_3$

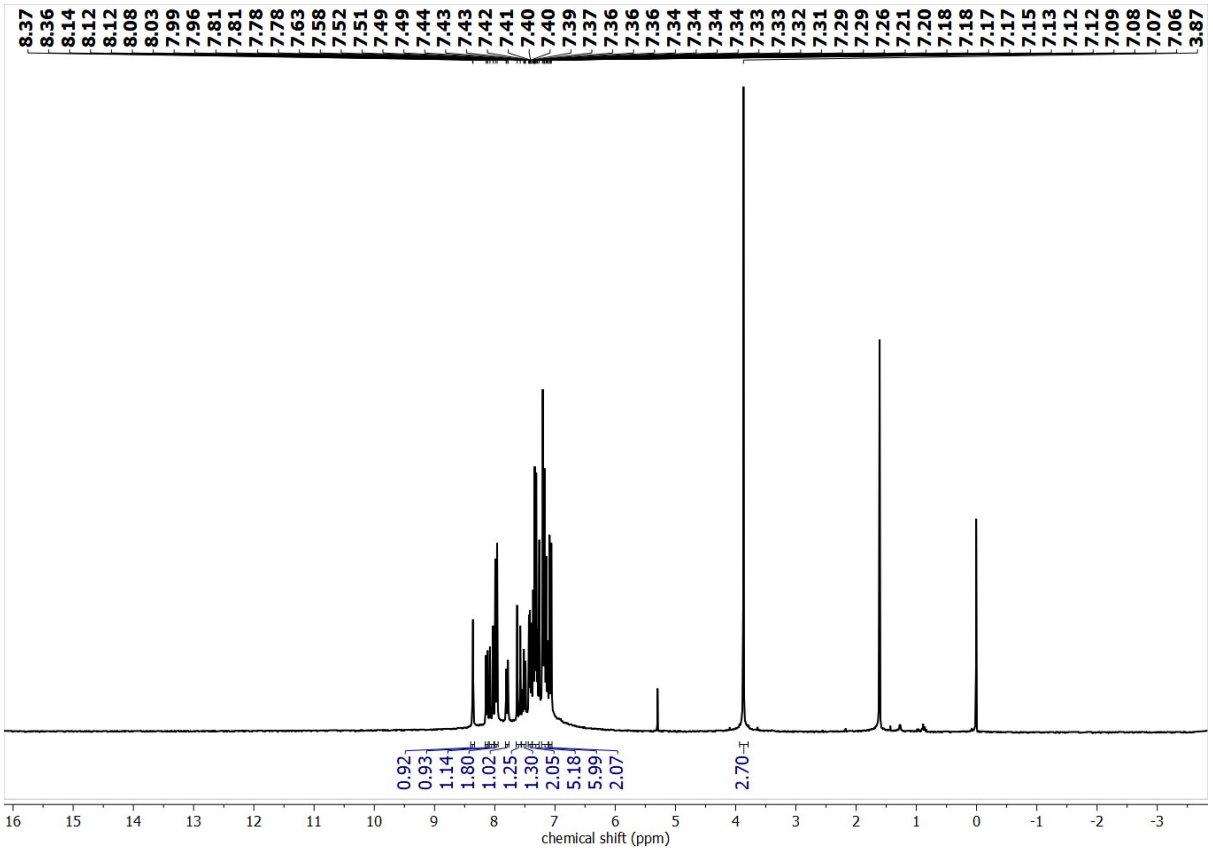


Figure S5: ^{1}H NMR of 2 in $CDCl_3$

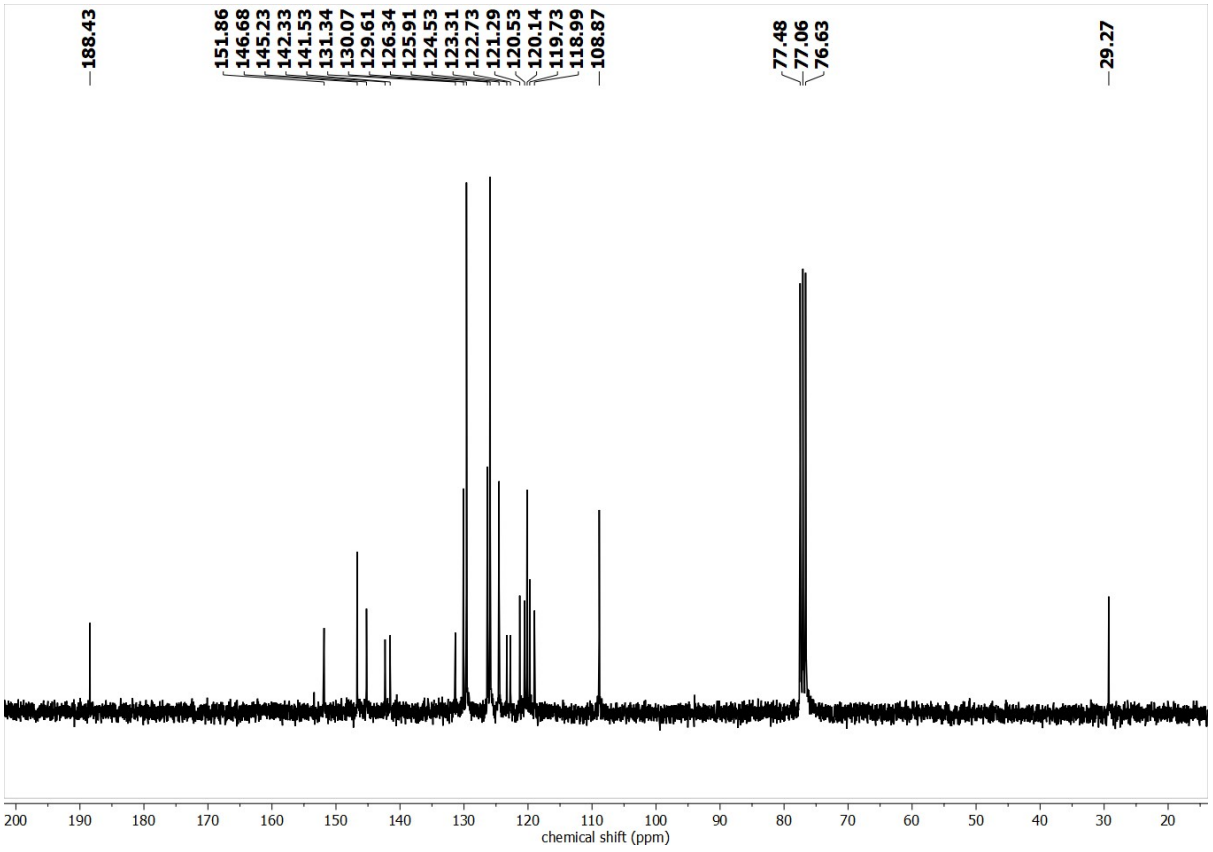


Figure S6: ^{13}C NMR of 2 in $CDCl_3$

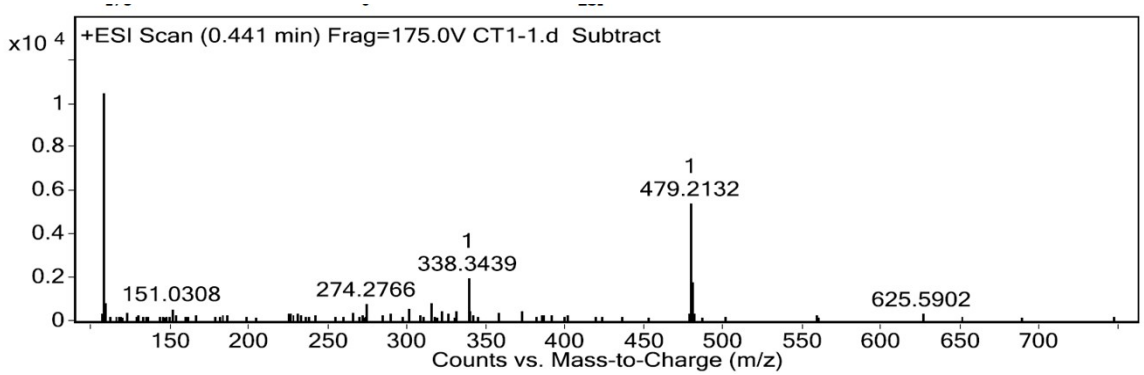


Figure S7: HRMS of 1

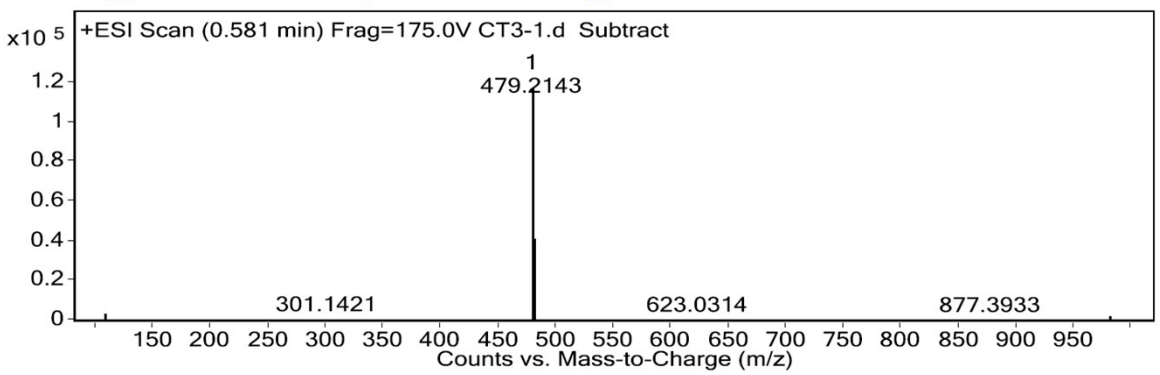


Figure S8: HRMS of 2

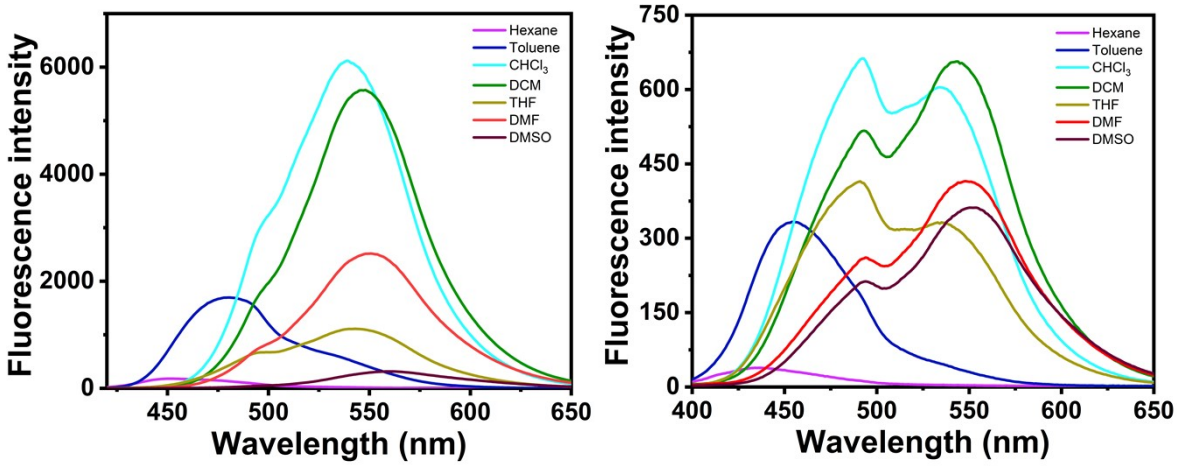


Figure S9: Fluorescence spectra of **1** (left, 2×10^{-5} M) and **2** (right, 2×10^{-5} M) in solvents of different polarity.

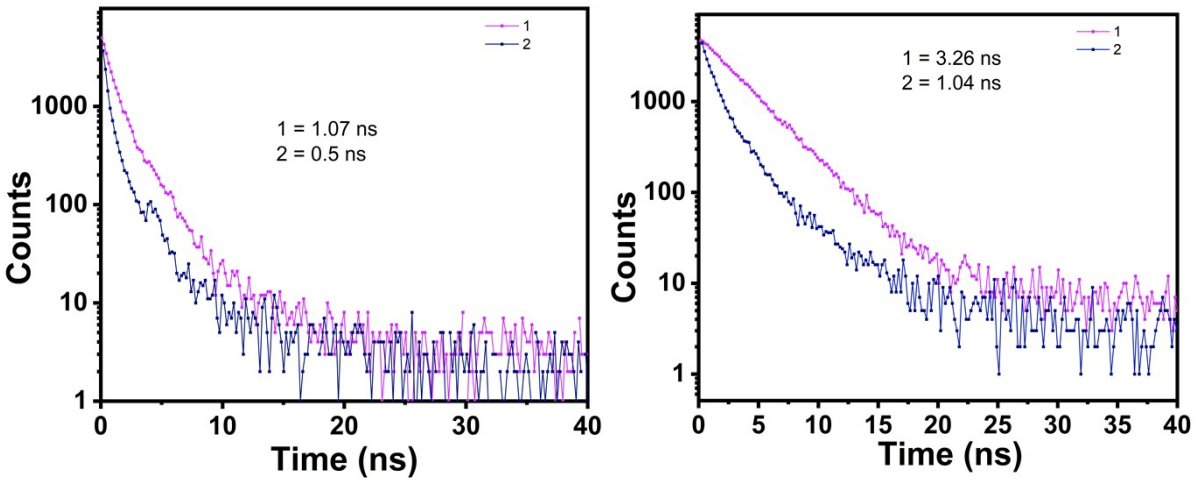


Figure S10: Fluorescence Lifetime decay curve of 1 & 2 in solid (left), chloroform solution ($2x10^{-5}$ M) (right)

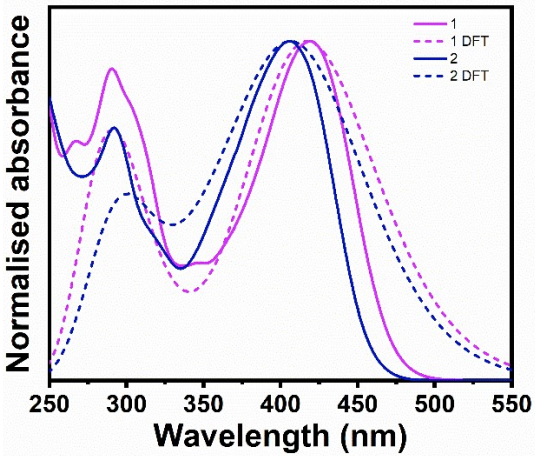
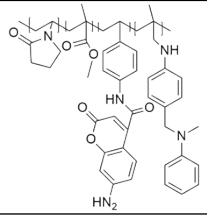
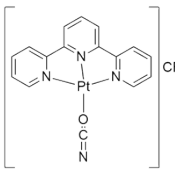
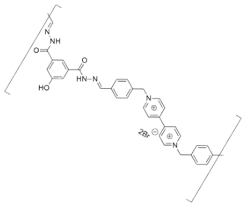
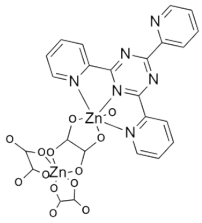
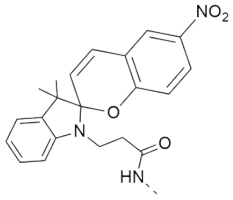
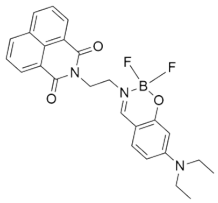
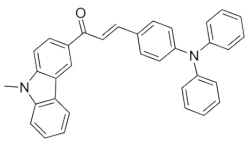


Figure S11: UV/Vis spectrum of 1 & 2 in chloroform ($2x10^{-5}$ M) (solid line) and DFT stimulated (dotted line).

Table S1: Comparison of the photophysical and vapochromic anticounterfeiting properties of the title compound with reported molecules.

Reference	Material	Vapour analyte	Color change	Substrate	Sensing Mechanism	Shift Type	Reversibility
1		$NaNO_2$ (Acid spray)	Colorless to multiple distinct color	Filter paper	Aza-coupling (Covalent bond forming)	Bathochromic 300nm – 380 nm to 432 nm to 523 nm (+ 52 – 143 nm increaced intensity)	Irreversible

2		MeCN / MeOH Vapour	Red to yellow	Banknote	Metal – ligand charge transfer	Hypsochromic 538 nm to 360 nm (-178 nm)	Reversible
3		Ammonia vapour	Orange to green	Paper	Intramolecular charge transfer	Bathochromic (430 nm to 598 (+168 nm increased intensity)	Reversible
4		Ethylene diamine vapor	Light Yellow to light pink	Fiber filter paper	Intramolecular electron transfer	Bathochromic Colorless to 400-600 nm (+200-400 nm new band with increased intensity)	Ireversible
5		TFA, HCl, HNO_3, CH_3COOH vapours	Colorless to Magenta, yellow and yellow green	Anodic aluminium oxide	Intramolecular structural transformation	Bathochromic 335 nm to 430-630 (+95 to +295)	Reversible
6		HCl, TFA vapours	Blue to green	Whatmann filter paper	Intramolecular charge transfer	Hypsochromic 413 to 353 nm (-60 nm)	Reversible
This work		BF_3OEt_2 Vapours	Colorless to bright blue	paper	Intramolecular structural transformation	Hypsochromic 418 nm to 272 nm (-146 nm greater intensity)	Reversible

Coordinates of molecular structure of 1 from DFT calculation

C	6.27454360	3.61911762	0.97107914
C	7.66908313	3.45833765	0.91981893
C	8.24688833	2.22701488	0.61532517
C	7.38995166	1.15201830	0.36653840
C	5.97853444	1.29818168	0.40711347
C	5.42547219	2.54528452	0.71528135
H	5.85660994	4.59209855	1.20998908

H	8.31264532	4.31042631	1.11752465
H	9.32557800	2.11768558	0.56946653
H	4.34764957	2.67583106	0.75231819
C	6.52245028	-0.87285430	-0.12961747
C	6.32592464	-2.21696973	-0.47334137
C	5.02208280	-2.67344109	-0.58215573
C	3.90532359	-1.83106583	-0.36592555
C	4.11905664	-0.48756806	-0.02940968
C	5.42133424	-0.00104103	0.08836409
H	7.16028735	-2.88617854	-0.65696599
H	4.81820848	-3.70536647	-0.84469904
H	3.28874394	0.18821396	0.14200907
C	9.03985721	-0.69287753	-0.11535279
H	9.71250335	-0.22818935	0.61005329
H	9.03953933	-1.76852178	0.06987835
H	9.42806783	-0.50871388	-1.12478847
N	7.70095669	-0.17019669	0.05673240
O	2.45142688	-3.64630995	-0.80344045
C	2.55056742	-2.45035531	-0.51957816
C	-1.18224127	-1.51232620	-0.34062707
C	-1.35034189	-0.16016467	0.02285548
C	-2.35046123	-2.26040361	-0.58226766
C	-2.60786595	0.40926332	0.13679602
H	-0.48101331	0.45317385	0.23884188
C	-3.61602178	-1.69878104	-0.48398215
H	-2.25607958	-3.30377399	-0.87115682
C	-3.76882892	-0.34888574	-0.12044856
H	-2.70546181	1.44756253	0.43354389
H	-4.49348082	-2.30042065	-0.69273324

N	-5.04920434	0.23438977	-0.01009071
C	-6.15732671	-0.53483224	0.45029756
C	-7.39233227	-0.46201721	-0.21143977
C	-6.03192758	-1.36329596	1.57613774
C	-8.48002340	-1.20036545	0.25079950
H	-7.49217309	0.17463630	-1.08419472
C	-7.12029785	-2.11152247	2.02013639
H	-5.08123464	-1.41610372	2.09608902
C	-8.35065544	-2.03220933	1.36453007
H	-9.42972992	-1.13356598	-0.27202508
H	-7.00792299	-2.74826997	2.89286000
H	-9.19823874	-2.61117129	1.71787986
C	-5.25471827	1.59830056	-0.36778163
C	-4.70337889	2.11710535	-1.54963142
C	-6.02187416	2.43740191	0.45462225
C	-4.90695078	3.45273304	-1.89080653
H	-4.11826830	1.46967229	-2.19423244
C	-6.23516381	3.76678173	0.09570787
H	-6.44713444	2.04116964	1.37062667
C	-5.67612567	4.28429208	-1.07442484
H	-4.47365848	3.83949190	-2.80866025
H	-6.83129659	4.40379728	0.74271956
H	-5.83888282	5.32229369	-1.34740712
C	0.11452931	-2.16048930	-0.47706064
H	0.09748860	-3.21909043	-0.73258426
C	1.34076707	-1.61446640	-0.33252624
H	1.45458824	-0.56495969	-0.08747829

Coordinates of molecular structure of 2 from DFT calculation

C	9.59670355	-1.88773319	-0.27705619
C	10.32839910	-0.72066731	-0.00011761
C	9.69216924	0.49529141	0.24216845
C	8.29583987	0.51691527	0.19551036
C	7.54091338	-0.65438517	-0.07549994
C	8.20518371	-1.86175310	-0.31532676
H	10.12393708	-2.81877763	-0.45998902
H	11.41301984	-0.76526920	0.03004055
H	10.26870198	1.38733690	0.46457576
H	7.64291664	-2.76687124	-0.52588856
C	6.12295702	1.12452103	0.26778141
C	4.91183669	1.81773148	0.39820244
C	3.73258360	1.11214797	0.21636670
C	3.71879154	-0.27372918	-0.08858054
C	4.94520474	-0.94906816	-0.20745289
C	6.14625944	-0.26501783	-0.02918646
H	4.88595019	2.87500531	0.64091409
H	2.79085908	1.64177413	0.31565251
H	4.94697192	-2.01095251	-0.43824948
C	7.81767219	2.93819589	0.71998162
H	8.75388585	3.18425264	0.21301203
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H	7.95575893	3.07288753	1.80004383
N	7.42315171	1.58658445	0.38425110
C	-1.31291623	-1.04908724	-0.31776507
C	-1.67508499	0.19010446	0.23469058
C	-2.34634691	-1.89777427	-0.75133039
C	-3.00760685	0.56732761	0.35164309

H	-0.91870307	0.86807562	0.61506750
C	-3.67773347	-1.52633457	-0.65727249
H	-2.06824977	-2.85477659	-1.17944739
C	-4.03424747	-0.28186323	-0.09982119
H	-3.26145869	1.52063076	0.80133839
H	-4.45364608	-2.19184293	-1.01892588
N	-5.38828140	0.10223321	0.00465963
C	-6.40038078	-0.87244466	0.24525959
C	-7.59334850	-0.84911331	-0.49268255
C	-6.22259834	-1.85801083	1.22827425
C	-8.58910524	-1.79210733	-0.24576032
H	-7.73222033	-0.09075739	-1.25597695
C	-7.21636522	-2.80801206	1.45542649
H	-5.30498737	-1.87488324	1.80678670
C	-8.40583053	-2.77899105	0.72469972
H	-9.50707706	-1.76179644	-0.82557250
H	-7.06383078	-3.56588157	2.21837162
H	-9.18060740	-3.51657537	0.90965427
C	-5.76637876	1.46985963	-0.12716967
C	-5.24065151	2.25944634	-1.16153806
C	-6.68178983	2.03988880	0.77044959
C	-5.61684009	3.59550503	-1.28380343
H	-4.53965582	1.81994702	-1.86321654
C	-7.06517865	3.37221703	0.62978243
H	-7.08853494	1.43313933	1.57253923
C	-6.53285226	4.15918536	-0.39316497
H	-5.20186933	4.19370826	-2.08990385
H	-7.77482253	3.79919863	1.33258466
H	-6.82914300	5.19848032	-0.49617949

C	0.09479141	-1.53502147	-0.46081739
C	1.21224919	-0.59517691	-0.21173302
H	0.98628540	0.44224864	0.00713384
C	2.48839011	-1.03020893	-0.28302144
H	2.61045968	-2.08661263	-0.51869674
O	0.30724011	-2.70296371	-0.79475248

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