Electronic Supplementary Material (ESI) for Faraday Discussions.

Supplementary Information

On the photophysics of butadiyne bridged pyrene-phenyl molecular conjugates: multiple emissive pathways through locally excited, intramolecular charge transfer, and excimer states

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Table of contents:

General experimental section:

Melting points were recorded using Sigma melting point apparatus in capillary tubes and were uncorrected. IR spectra were recorded on JASCO FT-IR-4100 spectrometer. ^{1}H (400 MHz, 500 MHz) and ^{13}C (100 MHz, 125 MHz) NMR spectra of the butadiynyl derivatives were recorded on Bruker Avance 400 spectrometer and Bruker Avance 500 spectrometer respectively. The chemical shifts (δ ppm) and coupling constants (Hz) were calculated with reference to chloroform. In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was ascertained by recording the DEPT-135 experiment and was mentioned in the parentheses. High resolution mass measurements were performed using Micromass Q-ToF ESI instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) were carried out on glass plates (7.5 x 2.5 and 7.5 x 5.0 cm) coated with Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates. Various combinations of ethyl acetate and hexane or dichloromethane and hexane were used as eluent. Visualization of spots was done by exposure to iodine vapor. All compounds were purified by silica gel [Acme's silica gel (100-200 mesh)] column chromatography.

Measurement of quantum yield:

The fluorescence quantum yield of the fluorophores **PyBP**, **PyBPOMe**, **PyBPCN**, and **PyBPNMe$_2$** was measured in cyclohexane following the equation given below.[1]

$$\phi_{unk} = \phi_{std} \times (F_{unk}/F_{std}) \times (A_{std}/A_{unk}) \times (n^2_{unk}/ n^2_{std}) \times (q_{std}/q_{unk})$$

The "unk" and "std" indicate unknown and standard respectively. The F_{unk}, F_{std} correspond to the integrated intensities under the corrected emission spectra of the derivatives, A_{unk}, A_{std}

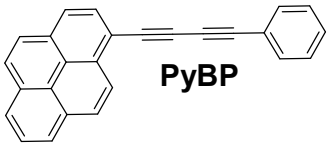
correspond to the optical densities of the solutions of the derivatives, n_{unk}, n_{std} indicate refractive indices of the solvents used and q_{std} and q_{unk} are the excitation light intensities at the excitation wavelengths taken from the lamp profile of the fluorometer. The excitation wavelength was 350 nm for both the reference and the samples. The absorbance values of all the samples were kept around 0.02. The fluorescence quantum yield was determined with reference to quinine sulphate (ϕ_f=0.546 in 1N H_2SO_4).[2]

General procedure for the preparation of butadiynyl derivatives:

To a magnetically stirred solution of alkyne A (1 mmol), alkyne B (5 mmol), $Cu(OAC)_2.H_2O$ (10 mol %) in CH_2Cl_2 inside a round bottom flask, piperidine (3 mmol) was added. The round bottom flux was then fitted with condenser. The reaction mixture was stirred for 12 hr. in open atmosphere at rt. The mixture was then concentrated under reduced pressure and the crude was purified on a silica gel column.

1-(4-phenylbuta-1,3-diynyl)pyrene (PyBP):

ethyl acetate-hexane (1: 24) as eluent to afford the diyne as a yellow solid (61%).



Physical appearance: yellow solid.

R_f: 0.5, (1:24, Ethyl acetate:Hexane)

m.p.: 179-181 ^oC

IR (neat): 3083, 2922, 2854, 2203, 2136, 1633, 1596, 1459, 1439, 1028, 842, 750, 684 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 9.2, 1H), 8.25-8.18 (m, 4H), 8.13-8.09 (m, 2H), 8.05-8.02 (m, 2H), 7.62 (d, *J* = 6, 2H), 7.40-7.35 (m, 3H).

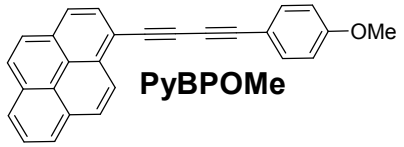
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 133.49 (1 x C), 132.69 (2 x CH), 132.04 (1 x C), 131.34 (1 x C), 131.17 (1 x C), 130.69 (1 x CH), 129.40 (1 x CH), 129.01 (1 x CH), 128.90 (1 x CH), 128.66 (2 x CH), 127.33 (1 x CH), 126.54 (1 x CH), 126.11 (1 x CH), 126.03 (1 x CH), 125.50 (1 x CH), 124.66 (1 x CH), 124.53 (1 x C), 124.32 (1 x C), 122.11 (1 x C), 116.25 (1 x C), 83.28 (1 x C), 81.19 (1 x C), 79.49 (1 x C), 74.51 (1 x C).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{26}H_{15}$ 327.1174, found 327.1180.

1-(4-(4-methoxyphenyl)buta-1,3-diynyl)pyrene (PyBPOMe):

ethyl acetate-hexane (1:9) as eluent to afford the diyne as a yellow solid (58%).

Physical appearance: yellow solid.



R_f: 0.5 (1:9, Ethyl acetate:Hexane)

m.p.: 163-165 ^oC

IR (neat): 3038, 3002, 2926, 2852, 2202, 2135, 1600, 1507, 1289, 1252, 1170, 1029, 842, 827, 713 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 8.8, 1H), 8.25-8.20 (m, 4H), 8.12-8.09 (m, 2H), 8.05-8.00 (m, 2H), 7.55 (d, *J* = 8.4, 2H), 6.90 (d, *J* = 8.4, 2H), 3.85 (s, 3H).

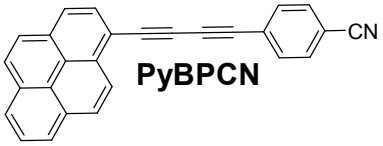
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 160.57 (1 x C), 134.32 (2 x CH), 133.38 (1 x C), 131.88 (1 x C), 131.33 (1 x C), 131.17 (1 x CH), 130.62 (1 x CH), 128.90 (1 x CH), 128.78 (1 x CH), 127.33 (2 x CH), 126.50 (1 x CH), 126.03 (1 x CH), 125.96 (1 x CH), 125.55 (1 x CH), 124.65 (1 x CH), 124.52 (1 x C), 124.31 (1 x C), 116.50 (1 x C), 114.37 (1 x CH), 113.98 (1 x C), 83.56 (1 x C), 80.63 (1 x C), 79.77 (1 x C), 73.34 (1 x C), 55.52 (1 x CH_3).

HRMS (ESI, M): m/z calcd. for $C_{26}H_{16}O$ 356.1201, found 356.1186.

4-(4-(pyren-1-yl)buta-1,3-diynyl)benzonitrile (PyBPCN):

Use of ethylacetate-hexane (1:9) as eluent furnished the diyne as yellow solid (65%).

Physical appearance: yellow solid.



R_f: 0.5, (1:9, Ethyl acetate:Hexane)

m.p.: 239-241 ^oC

IR (neat): 3171, 3127, 3040, 2922, 2853, 2226, 2208, 2146, 1601, 1508, 1405, 1184, 854, 829, 717, 548 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 8.57 (d, *J* = 9, 1H), 8.27-8.19 (m, 4H), 8.16-8.11 (m, 2H), 8.08-8.05 (m, 2H), 7.66 (s, 4H).

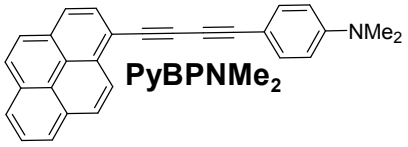
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 133.67 (1 x C), 133.04 (2 x CH), 132.40 (1 x C), 132.29 (2 x CH), 131.29 (1 x C), 131.07 (1 x C), 130.79 (1 x CH), 129.29 (1 x CH), 129.25 (1 x CH), 127.31 (1 x CH), 127.10 (1 x C), 126.67 (1 x CH), 126.32 (1 x CH), 126.28 (1 x CH), 125.25 (1 x CH), 124.70 (1 x CH), 124.49 (1 x C), 124.22 (1 x C), 118.45 (1 x C), 115.41 (1 x C), 112.47 (1 x C), 83.70 (1 x C), 81.04 (1 x C), 78.73 (1 x C), 77.72 (1 x C).

HRMS (ESI, M + Na^+): m/z calcd. for $C_{27}H_{13}NNa$ 374.0946, found 374.0953.

***N,N*-dimethyl-4-(4-pyren-1-yl)buta-1,3-diynyl)benzeneamine ($PyBPNMe_2$):**

Use of dichloromethane-hexane (1:4) as eluent yielded the diyne as yellow solid (55%).

Physical appearance: yellow solid.



R_f: 0.4, (1:4, Dichloromethane:Hexane)

m.p.: 129-131 ^oC

IR (neat): 3039, 2918, 2857, 2803, 2195, 2131, 1600, 1520, 1364, 1182, 836, 748, 508 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 8.8, 1H), 8.22-8.17 (m, 4H), 8.08-8.00 (m, 4H), 7.50 (d, *J* = 8.4, 2H), 6.68 (s, 2H), 3.01 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 150.60 (1 x C), 134.03 (2 x CH), 133.21 (1 x C), 131.64 (1 x C), 131.33 (1 x C), 131.12 (1 x C), 130.49 (1 x CH), 128.73 (1 x CH), 128.58 (1 x CH), 127.31 (2 x CH), 126.42 (1 x CH), 125.90 (1 x CH), 125.82 (1 x CH), 125.64 (1 x CH), 124.62 (1 x CH), 124.51 (1 x C), 124.32 (1 x C), 116.94 (1 x C), 112.03 (1 x CH), 85.20 (1 x C), 80.34 (2 x C), 79.77 (1 x C), 72.83 (1 x C), 40.33 (2 x CH_3).

HRMS (ESI, M + H^+): m/z calcd. for $C_{28}H_{20}N$ 370.1596, found 370.1599.

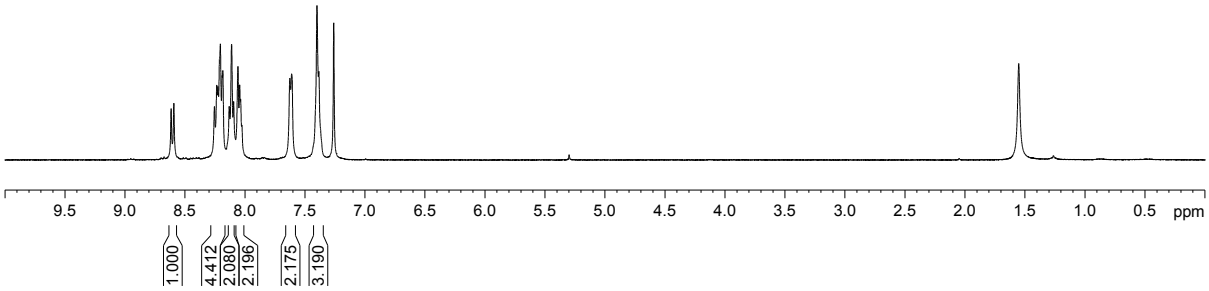


Fig. S1 ^{1}H NMR spectrum of **PyBP** in $CDCl_3$

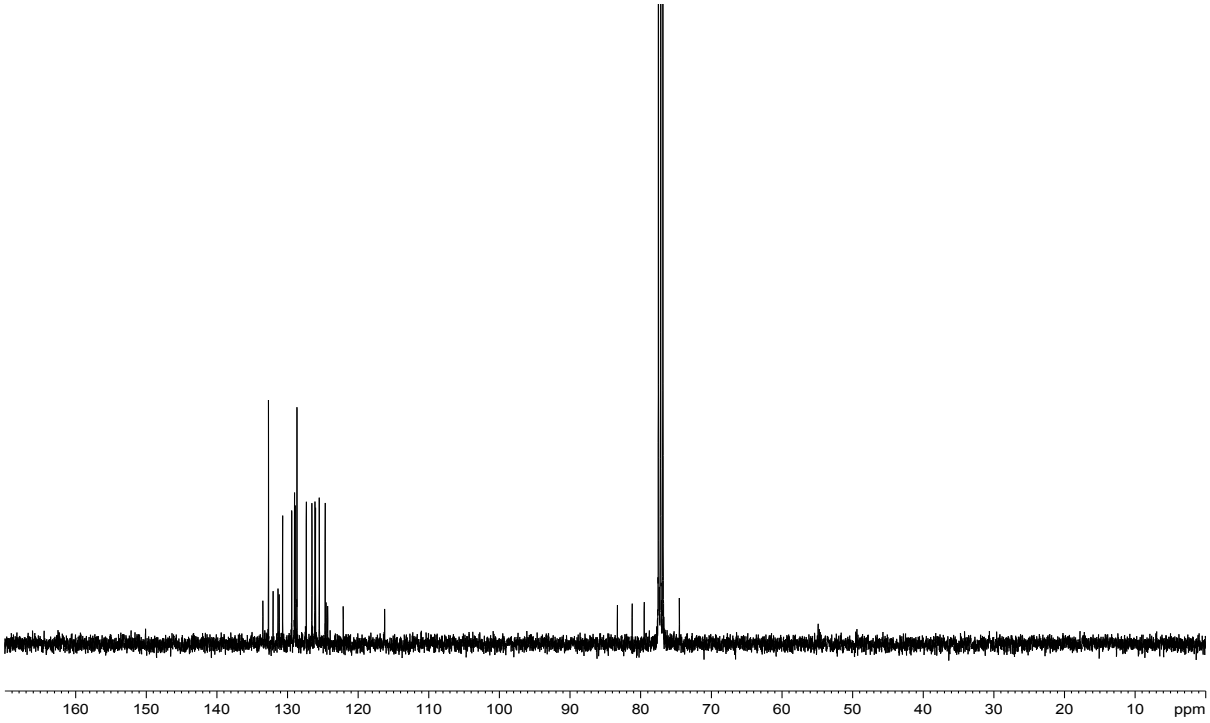


Fig. S2 ^{13}C NMR spectrum of **PyBP** in $CDCl_3$

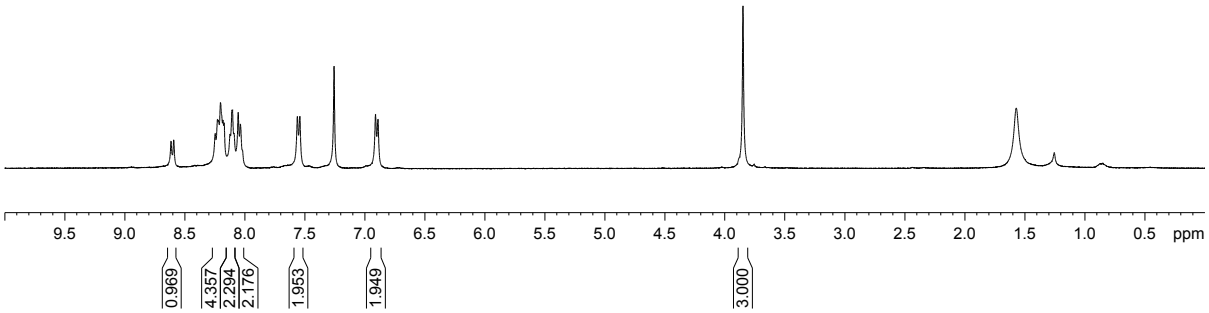


Fig. S3 ^{1}H NMR spectrum of **PyBPOMe** in $CDCl_3$

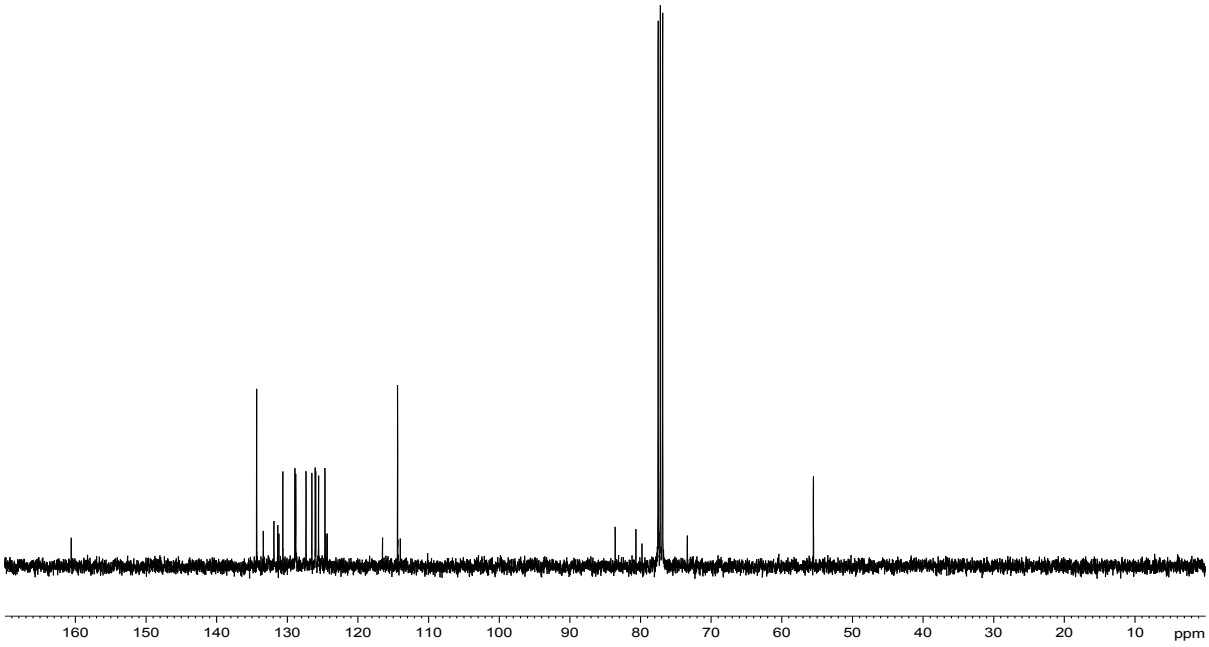


Fig. S4 ^{13}C NMR spectrum of **PyBPOMe** in $CDCl_3$

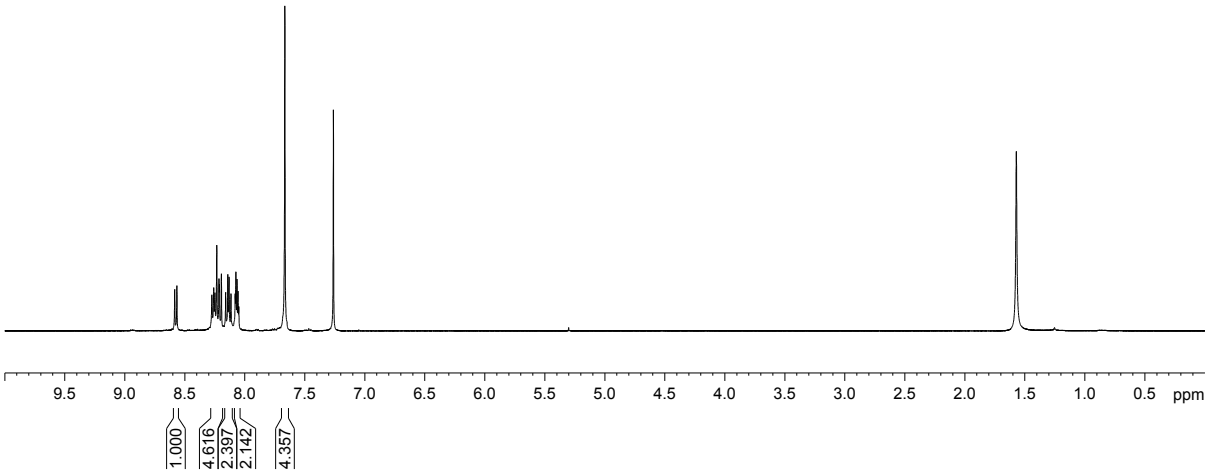


Fig. S5 ^{1}H NMR spectrum of **PyBPCN** in $CDCl_3$

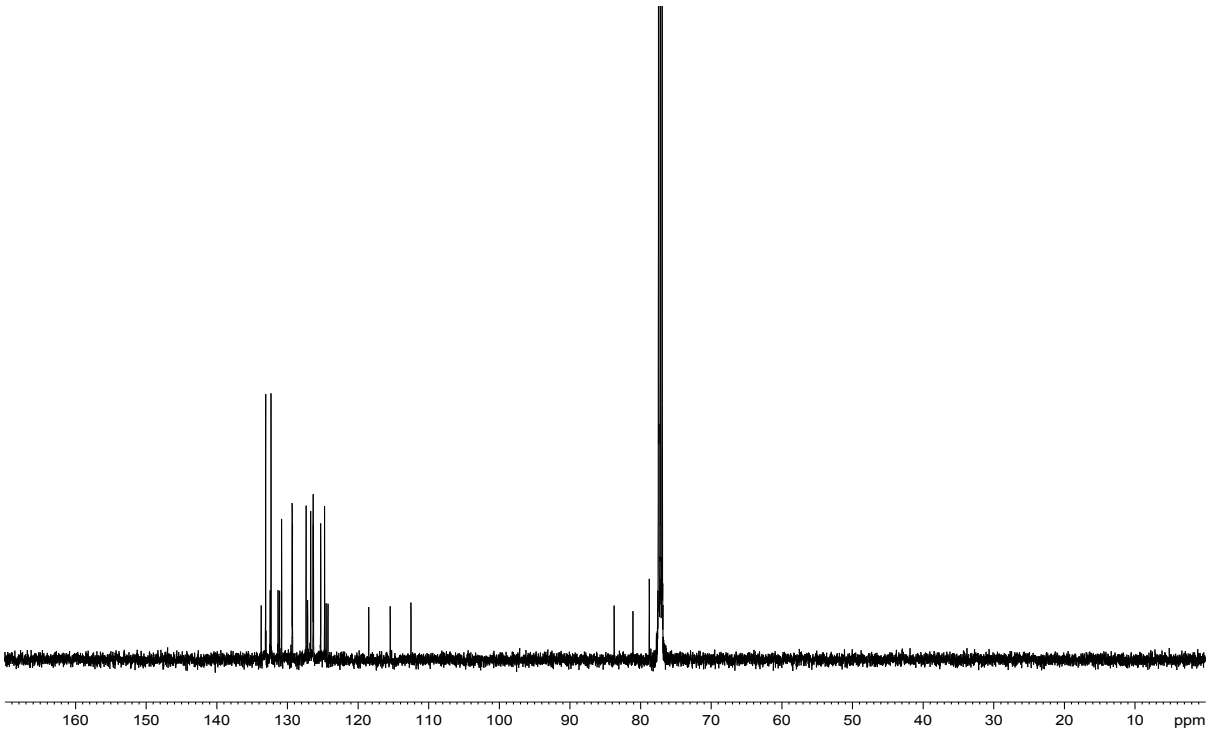


Fig. S6 ^{13}C NMR spectrum of **PyBPCN** in $CDCl_3$

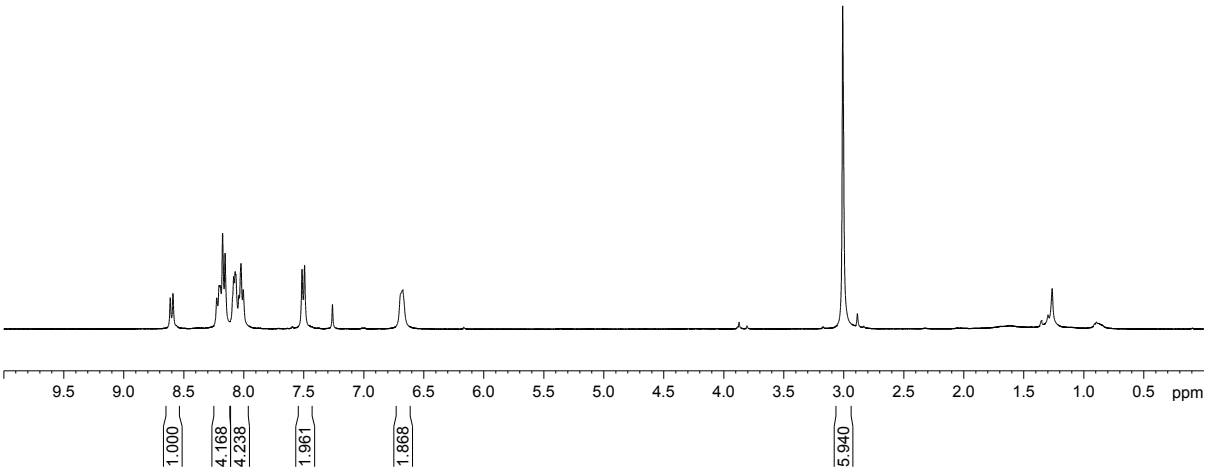


Fig. S7 ^{1}H NMR spectrum of **PyBPNMe$_2$** in $CDCl_3$

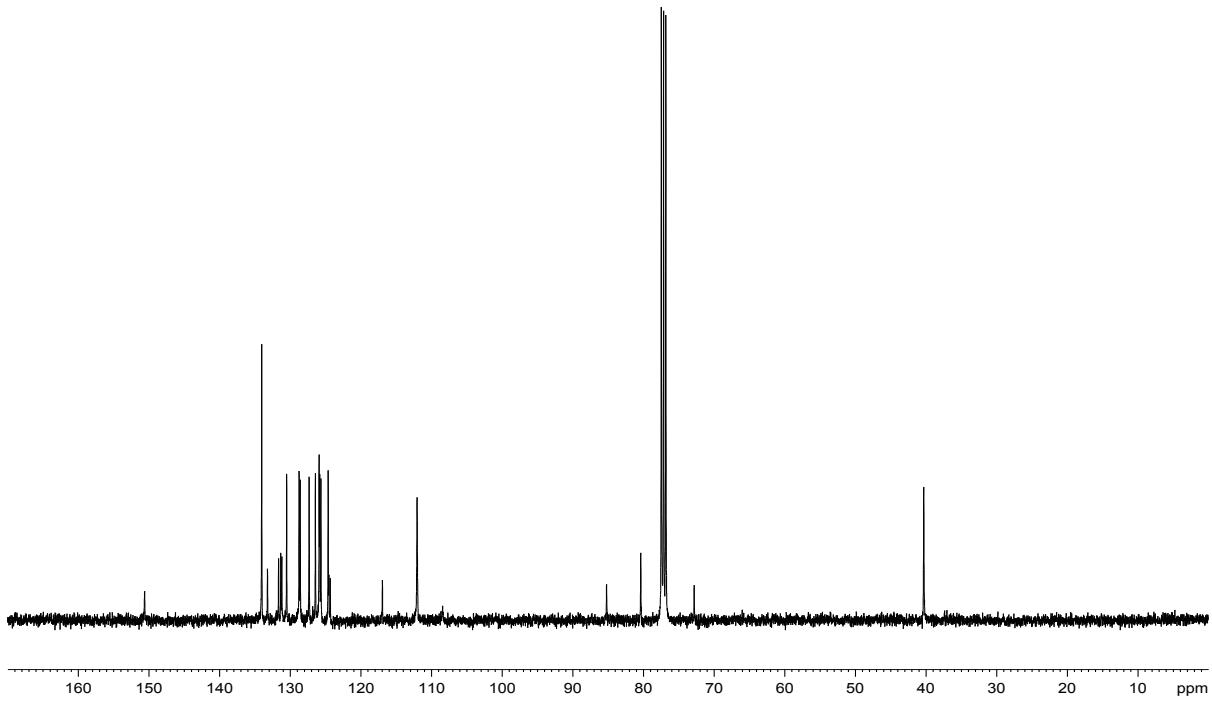


Fig. S8 ^{13}C NMR spectrum of **PyBPNMe$_2$** in $CDCl_3$

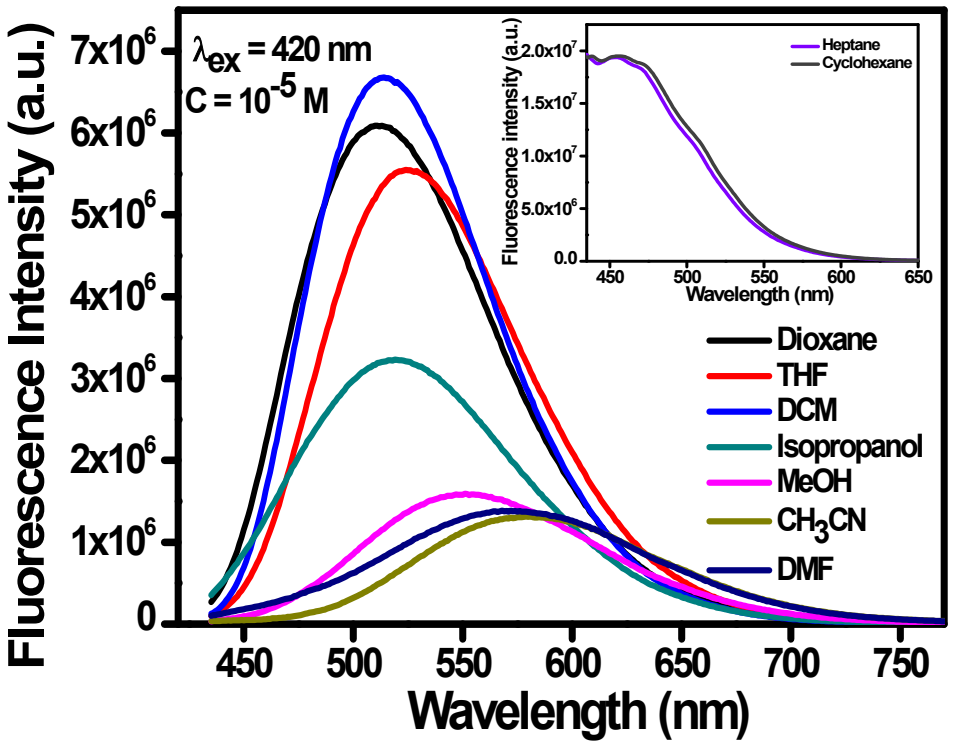


Fig. S9 Emission spectra of **PyBPNMe$_2$** at λ_{ex} =420 nm (C = 10^{-5} M, slit width =3 nm)

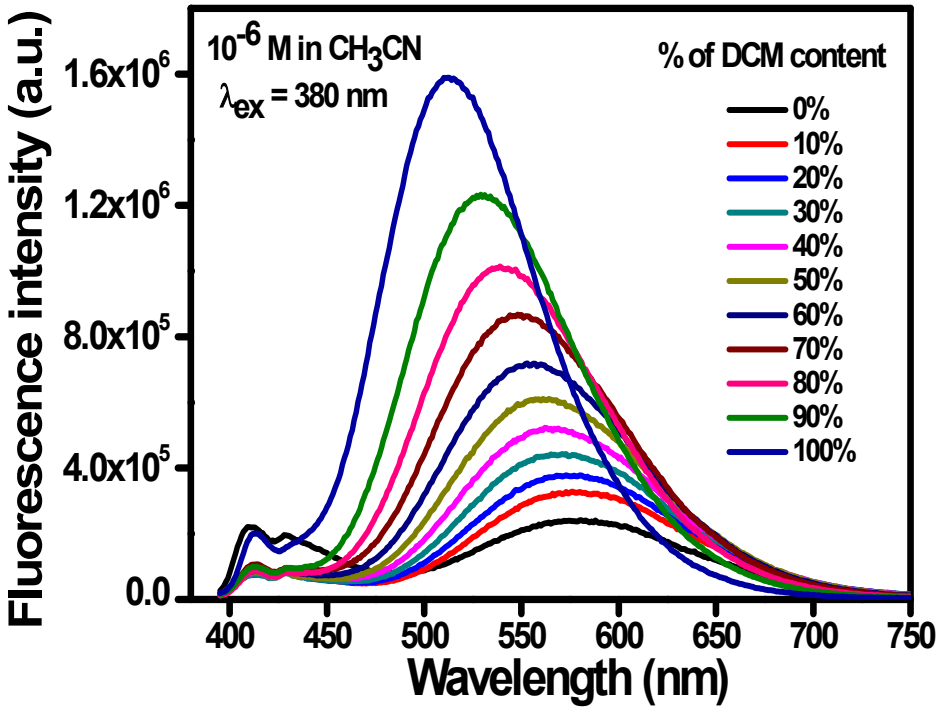


Fig. S10 Emission spectra of **PyBPNMe$_2$** in DCM-CH_3CN mixtures at λ_{ex} =380 nm (slit width = 3 nm)

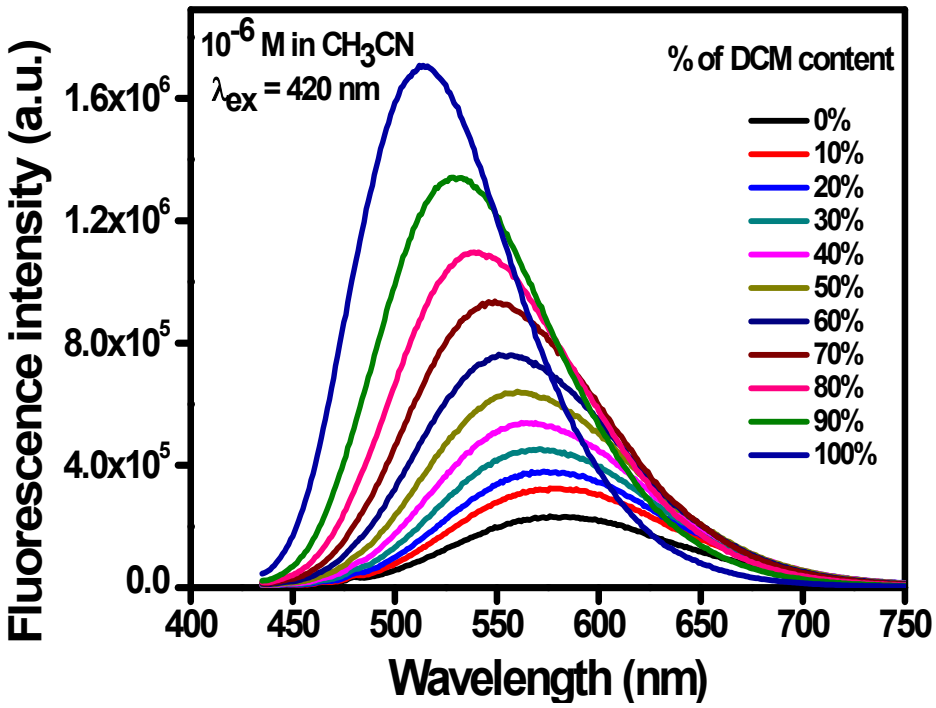


Fig. S11 Emission spectra of **PyBPNMe$_2$** in DCM-CH_3CN mixtures at λ_{ex} = 420 nm (slit width = 3 nm)

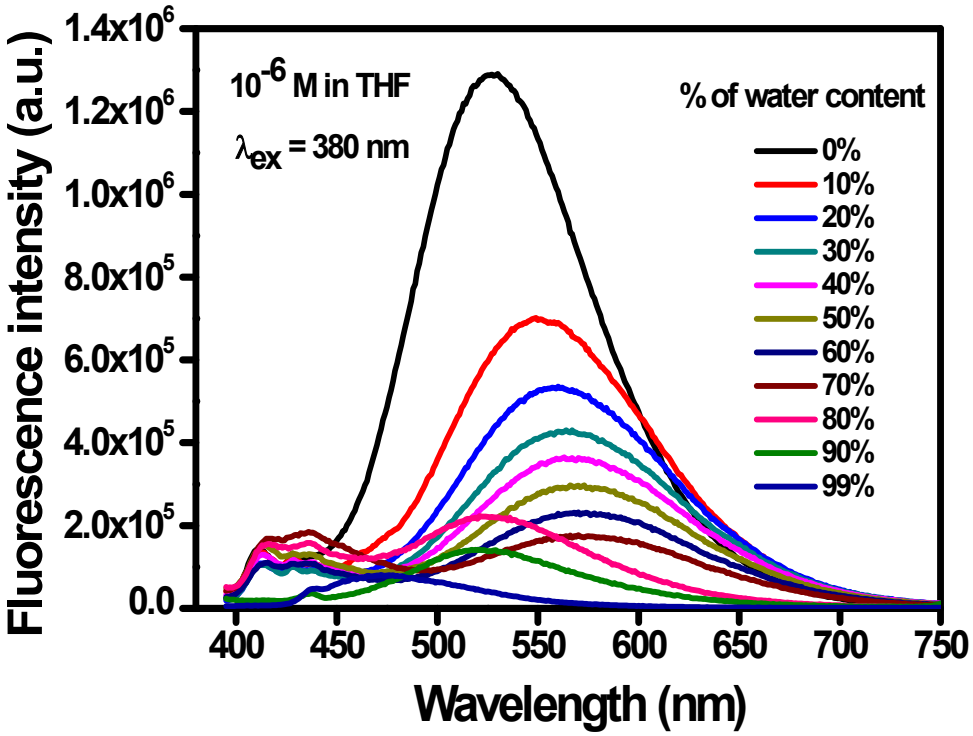


Fig. S12 Emission spectra of **PyBPNMe$_2$** in water-THF mixtures at λ_{ex} = 380 nm (Slit width = 3 nm)

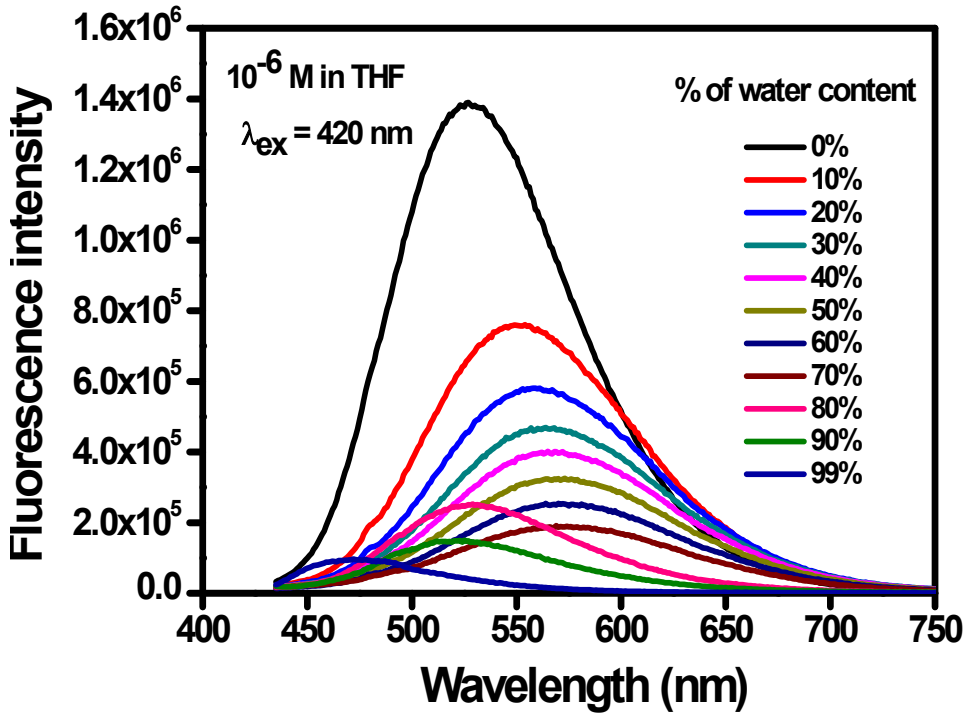


Fig. S13 Emission spectra of **PyBPNMe$_2$** in water-THF mixtures at λ_{ex} = 420 nm (Slit width = 3 nm)

Cartesian coordinates of the butadiynyl derivatives in CH_3CN:

Cartesian coordinates of **PyBP**

6	-0.993222	-2.574977	0.000254
6	-0.579470	-1.227576	0.000228
6	-1.556292	-0.193093	0.000125
6	-2.937360	-0.548674	0.000036
6	-3.329518	-1.920905	0.000050
6	-2.334195	-2.912889	0.000164
6	-1.205411	1.197041	0.000117
6	-3.935400	0.471234	-0.000063
6	-3.555638	1.845398	-0.000066
6	-2.158157	2.168087	0.000028
6	-4.554369	2.831643	-0.000158

1	-4.265213	3.876883	-0.000156
6	-5.900654	2.479115	-0.000249
6	-6.281583	1.140066	-0.000251
6	-5.318493	0.119541	-0.000158
6	-5.676578	-1.270577	-0.000151
6	-4.726497	-2.243976	-0.000050
1	-5.012953	-3.289960	-0.000042
1	-6.729141	-1.532437	-0.000227
1	-0.155913	1.465515	0.000188
1	-0.238845	-3.352096	0.000345
1	-2.626268	-3.957027	0.000185
1	-1.869288	3.213571	0.000027
1	-6.659111	3.253427	-0.000318
1	-7.332943	0.874070	-0.000324
6	0.803993	-0.928593	0.000315
6	1.998747	-0.691272	0.000344
6	3.327772	-0.423624	0.000261
6	4.520607	-0.181495	0.000170
6	5.911034	0.106382	0.000006
6	6.858172	-0.936504	-0.000622
6	6.362611	1.440847	0.000570
6	8.217340	-0.646507	-0.000786
1	6.516865	-1.964505	-0.001004
6	7.724259	1.718377	0.000394
1	5.638931	2.246783	0.001107

6	8.654938	0.678570	-0.000325
1	8.937526	-1.456429	-0.001276
1	8.060671	2.748654	0.000822

Cartesian coordinates of **PyBPOMe**

6	1.993300	-2.571557	-0.072273
6	1.541593	-1.246289	-0.022123
6	2.458200	-0.197976	0.111254
6	3.812643	-0.491602	0.110792
6	4.238562	-1.810737	0.114599
6	3.307883	-2.844883	0.030547
6	2.033933	1.120573	0.179343
6	4.736394	0.521821	0.068970
6	4.305951	1.831478	0.014764
6	2.942241	2.120680	0.107116
6	5.236740	2.865140	-0.132904
1	4.904289	3.878069	-0.202620
6	6.613619	2.563754	-0.183005
6	7.036550	1.237491	-0.066226
6	6.088154	0.217806	0.066533
6	6.502457	-1.105215	0.188553
6	5.595232	-2.103738	0.191304
1	5.928869	-3.108029	0.248161
1	7.530790	-1.343018	0.274882
1	0.996892	1.341355	0.267034
1	1.296368	-3.371201	-0.180885

1	3.632830	-3.859286	0.036423
1	2.608154	3.127452	0.118228
1	7.339644	3.340018	-0.307143
1	8.077406	1.011807	-0.086200
6	0.161604	-1.034059	-0.088435
6	-1.004825	-0.829740	-0.117837
6	-2.336277	-0.595506	-0.150678
6	-3.569430	-0.378233	-0.180970
6	-4.948699	-0.131073	-0.214436
6	-5.850690	-1.194056	-0.315310
6	-5.418079	1.192328	-0.194152
6	-7.222337	-0.949739	-0.324055
1	-5.489365	-2.198416	-0.372159
6	-6.796486	1.444016	-0.191773
1	-4.727552	2.003881	-0.185621
6	-7.702741	0.369444	-0.258970
1	-7.900926	-1.764488	-0.375129
1	-7.158460	2.454953	-0.135517
8	-9.110875	0.613514	-0.250690
6	-9.592345	0.619277	1.096625
1	-10.644936	0.783388	1.097118
1	-9.379937	-0.321184	1.563676
1	-9.105947	1.400160	1.641735

Cartesian coordinates of **PyBPCN**

6	0	1.775208	-2.592688	-0.000212
6	0	1.328008	-1.256933	-0.000200
6	0	2.280331	-0.200931	-0.000105
6	0	3.669245	-0.521540	-0.000025
6	0	4.094704	-1.883011	-0.000039
6	0	3.123592	-2.897397	-0.000133
6	0	1.894789	1.179323	-0.000088
6	0	4.641475	0.522264	0.000071
6	0	4.227500	1.886011	0.000086
6	0	2.822797	2.172794	0.000003
6	0	5.201403	2.895611	0.000180
1	0	4.885967	3.933499	0.000192
6	0	6.555384	2.577775	0.000258
6	0	6.969081	1.249519	0.000244
6	0	6.032519	0.205690	0.000151
6	0	6.424038	-1.174582	0.000134
6	0	5.498645	-2.170349	0.000044
1	0	5.811161	-3.209262	0.000032
1	0	7.483043	-1.410371	0.000196
1	0	0.838062	1.417402	-0.000149
1	0	1.037778	-3.385912	-0.000284
1	0	3.441423	-3.934410	-0.000145
1	0	2.508142	3.211146	0.000015
1	0	7.294255	3.371138	0.000331

1	0	8.026992	1.009552	0.000306
6	0	-0.061867	-0.992527	-0.000282
6	0	-1.261899	-0.787963	-0.000324
6	0	-2.597188	-0.557954	-0.000280
6	0	-3.795723	-0.350823	-0.000227
6	0	-5.193557	-0.106943	-0.000099
6	0	-6.108117	-1.177507	0.000550
6	0	-5.689704	1.210736	-0.000728
6	0	-7.475263	-0.931965	0.000672
1	0	-5.731577	-2.193115	0.000952
6	0	-7.058774	1.444850	-0.000600
1	0	-4.990366	2.037868	-0.001312
6	0	-7.955898	0.377147	0.000154
1	0	-8.169028	-1.765023	0.001174
1	0	-7.427930	2.464177	-0.001089
6	0	-9.472805	0.642840	0.000292
7	0	-10.602211	0.840660	0.000395

Cartesian coordinates of **PyBPNMe$_2$**

6	2.347758	-2.569820	-0.077827
6	1.915648	-1.231029	-0.070807
6	2.872126	-0.181359	-0.043692
6	4.259428	-0.514234	-0.019273
6	4.673333	-1.879612	-0.023894
6	3.696569	-2.887927	-0.054545
6	2.497949	1.204101	-0.038910

6	5.241593	0.521895	0.010707
6	4.838775	1.888826	0.014443
6	3.435151	2.189443	-0.011793
6	5.820219	2.892208	0.044186
1	5.514594	3.933033	0.047087
6	7.172634	2.561401	0.070606
6	7.576105	1.228141	0.067594
6	6.629382	0.192562	0.037542
6	7.010929	-1.192679	0.032655
6	6.077211	-2.180791	0.002995
1	6.377852	-3.222962	-0.000693
1	8.068353	-1.434466	0.052699
1	1.443356	1.452215	-0.057570
1	1.607836	-3.360242	-0.099554
1	4.005885	-3.927367	-0.058904
1	3.132782	3.231269	-0.008556
1	7.918047	3.348235	0.093849
1	8.631854	0.980137	0.088250
6	0.530490	-0.954501	-0.089455
6	-0.667909	-0.740515	-0.101465
6	-1.991473	-0.527670	-0.116375
6	-3.194163	-0.343074	-0.122349
6	-4.590471	-0.131219	-0.007626
6	-5.205951	-0.092968	1.255679
6	-5.385329	0.039731	-1.156185

6	-6.578671	0.110488	1.361121
1	-4.605825	-0.221134	2.148145
6	-6.756261	0.240195	-1.040080
1	-4.923134	0.012073	-2.135404
6	-7.366931	0.276166	0.220054
1	-7.053302	0.142706	2.334837
1	-7.351319	0.369256	-1.936941
7	-8.790449	0.473516	0.390773
6	-9.538779	-0.744529	0.027034
1	-10.570346	-0.651305	0.374059
1	-9.551057	-0.912686	-1.059798
1	-9.085469	-1.610800	0.508679
6	-9.282471	1.623844	-0.386029
1	-10.301720	1.855066	-0.069255
1	-8.651087	2.491488	-0.194548
1	-9.295494	1.428439	-1.467658

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1. C. A. Parker, Photoluminescence of Solutions, Elsevier Publishing Company, Amsterdam, **1968**.
2. D. F. Eaton, *Pure & Appl. Chem*., 1988, **60**, 1107-1114.