Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPLEMENTARY INFORMATION

Synthesis, characterization and investigation of photophysical and photochemical properties of highly soluble novel metal-free, zinc(II), and indium(III) phthalocyanines substituted with 2,3,6-trimethylphenoxy moieties

Ekrem Gürel[a], Mehmet Pişkin [b], Selçuk Altun[a**], Zafer Odabaş[a], Mahmut Durmuş [c*]

[a]*Marmara University, Department of Chemistry, Kadıköy, 34722, Istanbul, Turkey*

[b]*Çanakkale Onsekiz Mart University, Vocational School of Technical Sciences, Department of Food Technology, Çanakkale, 17100, Turkey*

[c] *Gebze Technical University, Department of Chemistry, P.O. Box 141, Gebze, 41400, Kocaeli, Turkey*

1. Experimental

1.1. Materials

All chemicals used were of reagent grade quality. 3-nitrophthalonitrile, 4-nitrophthalonitrile, 3-(2,3,6-trimethylphenoxy)phthalonitrile (**1**) and 4-(2,3,6-trimethylphenoxy)phthalonitrile (**2**) were synthesized and purified according to the methods described previously in literature respectively [1-4]. Phthalonitrile, 2,3,6-trimethylphenol, 1,3-diphenylisobenzofuran (DPBF) and metal salts were purchased from Alfa Aesar, Fluka or Merck and used as received. The solvents were purified, dried and stored over molecular sieves (4Å). All reactions were carried out under dry argon atmosphere unless otherwise noted. The Pc compounds were purified successively by washing with hot acetic acid, water, ethanol and acetonitrile in the Soxhlet apparatus. Column chromatography was performed on silica gel 60 for a proper purification. Melting points of the Pc compounds were found to be higher than 300 ^{o}C. The homogeneity of the products was tested in each step by thin layer chromatography (Kieselgel F-254 percolated TLC plate).

1.2. Equipment

IR spectra were recorded on a Perkin Elmer Spectrum One FTIR (ATR sampling accessory) spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian UNITY INOVA 500 MHz spectrometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK, Marmara Research Centre. Mass spectra were acquired on Microflex MALDI-TOF mass spectrometer (Bruker Daltonics MS Germany) equipped with a nitrogen UV-Laser operating at 337 nm and spectra were recorded in reflectron mode with average of 50 shots. 2,5-dihydroxybenzoicacid (DHB) was prepared in chloroform ($CHCl_3$) at a concentration of 15 mg/mL as matrix. Matrix-assisted laser desorption/ionization (MALDI) samples were prepared by mixing sample solutions (1 mg/mL in $CHCl_3$) and the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf® micro tube. Finally, 0.5 μL of this mixture was deposited on the sample plate, dried at room temperature, and then analyzed.

Optical spectra in the UV-*Vis* region were recorded with a Perkin Elmer Lambda 25 spectrophotometer and a Shimadzu 2101 UV/*Vis* spectrophotometer. Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC) (Horiba Fluorolog 3 equipment.) Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvette at room temperature. Photo-irradiations were done using a General Electric quartz line lamp (300W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations respectively. An interference filter (Intor, 670 nm and 700 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter.

1.3. Photophysical parameters

1.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using (Equation 1) [5-6].

$$\Phi_F = \Phi_F(\mathrm{Std})\frac{F \, . \, A_{\mathrm{Std}} \, . \, n^2}{F_{\mathrm{Std}} \, . \, A \, . \, n^2_{\mathrm{Std}}} \qquad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**In(OAc)Pc**, **3-8**) and the standard (**ZnPc**), respectively. A and A_{Std} are the relative absorbance of the samples and standard at the excitation wavelength, respectively. n^2 and n^2_{Std} are the refractive indices of solvents for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) (Φ_F = 0.20) [7] was employed as the standard. Both the sample and standard were excited at the same wavelength. The absorbance of the solutions was ranged between 0.04 and 0.05 at the excitation wavelength.

Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC). The natural radiative lifetimes (τ_0) were evaluated using Equation 2 [8].

$$\tau_0 = \frac{\tau_F}{\phi_F} \qquad (2)$$

1.4. Photochemical parameters

1.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in literature [9]. Typically, a 3 mL portion of the respective unsubstituted, peripherally and non-peripherally tetra-substituted In(III)Pcs, Zn(II)Pcs and metal free Pcs solutions (concentration = 1×10^{-5} M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in the reference. [9]. Φ_Δ

values were determined in air using the relative method with unsubstituted ZnPc (in DMF) as references. DPBF was used as chemical quenchers for singlet oxygen in DMF. The Φ_Δ values of the studied ZnPc complexes were calculated using equation 3:

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{R \,.\, I_{abs}^{Std}}{R^{Std} \,.\, I_{abs}} \qquad (3)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yields for the standard. Unsubstituted ZnPc (Φ_Δ^{Std} = 0.56 in DMF) [10] was used as standard. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**In(OAc)Pc**, **3-8**) and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples and standards, respectively. I_{abs} was determined by using equation 4.

$$I_{abs} = \frac{\alpha . S . I}{N_A} \qquad (4)$$

To avoid chain reactions induced by DPBF in the presence of singlet oxygen [11], the concentration of quenchers (DPBF) was lowered to ~ 3 × 10^{-5} M. Solutions of sensitizer (concentration = 1×10^{-5} M) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described in literature [9]. DPBF degradation at 417 nm was monitored. The light intensity used for Φ_Δ determinations was found to be 6.60 x 10^{15} photons s^{-1} cm^{-2}.

1.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature [9]. Photodegradation quantum yields were determined using equation 5,

$$\Phi_d = \frac{(C_0 - C_t) \, . \, V \, . \, N_A}{I_{abs} \, . \, S \, . \, t} \qquad (5)$$

where C_0 and C_t are the samples (**In(OAc)Pc**, **3-8**) concentrations before and after irradiation respectively, V is the reaction volume, N_A is the Avogadro's constant, S is the irradiated cell area, t is the irradiation time and I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**In(OAc)Pc**, **3-8**). A light intensity of 2.15×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

References

[1] R.D. George, A.W. Snow, Synthesis of 3-nitrophthalonitrile and tetra-α-substituted phthalocyanines, J. Heterocycl. Chem. 32 (1995) 495–498.

[2] J.G. Young, W. Onyebuagu, Synthesis and Characterization of Di-disubstituted Phthalocyanines, J. Org. Chem. 55 (1990) 2155–2159.

[3] Z. Odabaş, E.B. Orman, M. Durmuş, F. Dumludağ, A.R. Özkaya, M. Bulut, Novel alpha-7-oxy-4-(4-methoxyphenyl)-8-methylcoumarin substituted metal-free, Co(II) and Zn(II) phthalocyanines: Photochemistry, photophysics, conductance and electrochemistry, Dyes Pigm. 95 (2012) 540–552.

[4] Z. Odabaş, H. Kara, A.R. Özkaya, M. Bulut, Synthesis, characterization and electrochemical properties of novel beta 7-oxy-4-(4-methoxyphenyl)-8-methylcoumarin substituted metal-free, Zn(II) and Co(II) phthalocyanines, Polyhedron, 39 (2012) 38–47.

[5] S. Fery-Forgues, D. Lavabre, Are fluorescence quantum yields so tricky to measure? A demonstration using familiar stationery products, J. Chem. Educ. 76 (1999) 1260–1264.

[6] D. Maree, T. Nyokong, K. Suhling, D. Phillips, Effects of axial ligands on the photophysical properties of silicon octaphenoxyphthalocyanine, J. Porphy. Phthalocyan. 6 (2002) 373–375.

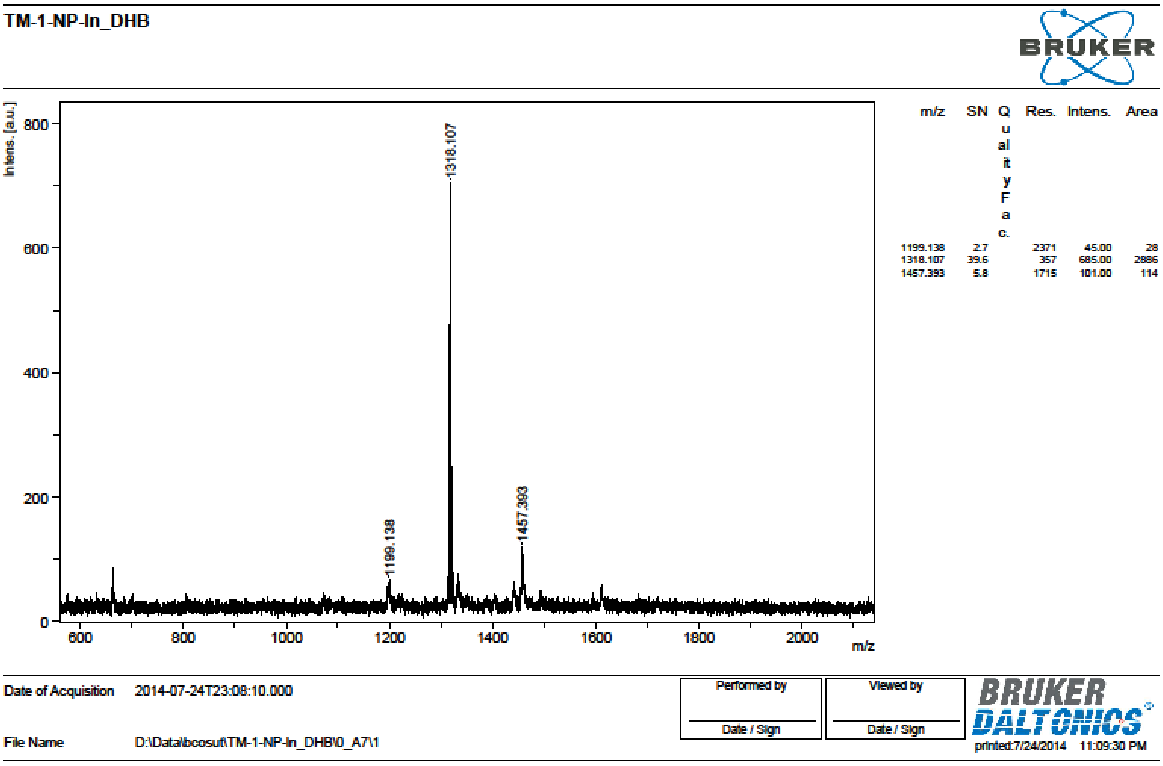
[7] A. Ogunsipe, J.-Y. Chen, T. Nyokong, Photophysical and photochemical studies of Zinc(II) phthalocyanine derivatives – effects of substituents and solvents, New J. Chem. 28 (2004) 822–827.

[8] C.D. Geddes, J.R. Lakowicz, Topics in Fluorescence Spectroscopy, Springer, New York, 2005. p. 1.

[9] M. Durmuş, Photochemical and Photophysical Characterization, in: T .Nyokong, V. Ahsen (Eds.), Photosensitizers in Medicine, Environment, and Security, Springer, NewYork, 2012, pp.141.

[10] Y. Zorlu, F. Dumoulin, M. Durmuş, V. Ahsen, Comparative studies of photophysical and photochemical properties of solketal substituted platinum (II) and zinc (II) phthalocyanine sets, Tetrahedron 66 (2010) 3248-3258.

[11] W. Spiller, H. Kliesch, D. Wohrle, S. Hackbarth, B. Roder, G. Schnurpfeil, Singlet Oxygen Quantum Yields of Different Photosensitizers in Polar Solvents and Micellar Solutions, J. Porphy. Phthalocyan. 2 (1998) 145–158.



TM-1-NP-In_DHB

m/z	SN	Quality Fac.	Res.	Intens.	Area
1199.138	2.7		2371	45.00	28
1318.107	39.6		357	685.00	2886
1457.393	5.8		1715	101.00	114

Date of Acquisition 2014-07-24T23:08:10.000

File Name D:\Data\bcosut\TM-1-NP-In_DHB\0_A7\1

Performed by

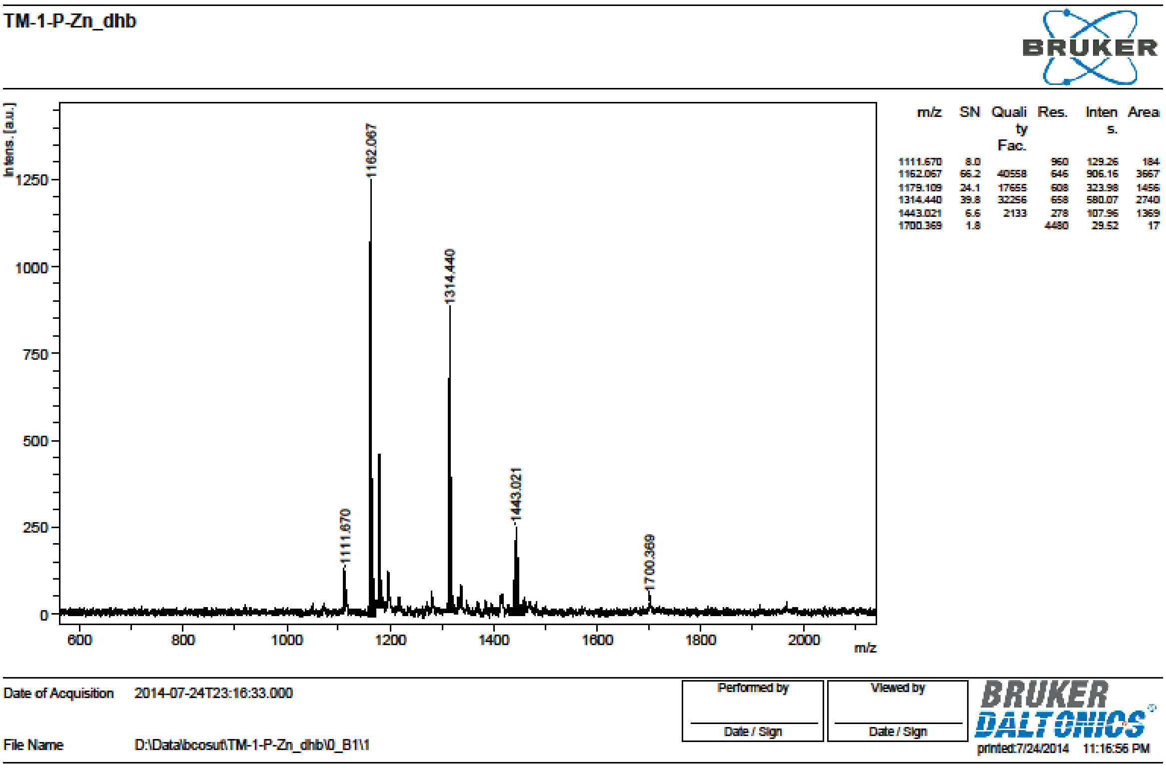
Date / Sign

Viewed by

Date / Sign

printed:7/24/2014 11:09:30 PM

Fig. S1. Positive ion in reflectron mode MALDI-TOF mass spectrum of compound **3** were obtained in 2,5-dihydroxybenzoicacid.



TM-1-P-Zn_dhb

m/z	SN	Quality Fac.	Res.	Intens.	Area
1111.670	8.0		960	129.26	184
1162.067	66.2	40558	646	906.16	3667
1179.109	24.1	17655	608	323.98	1456
1314.440	39.8	32256	658	580.07	2740
1443.021	6.6	2133	278	107.96	1369
1700.369	1.8		4480	29.52	17

Date of Acquisition 2014-07-24T23:16:33.000

File Name D:\Data\bcosut\TM-1-P-Zn_dhb\0_B1\1

Performed by

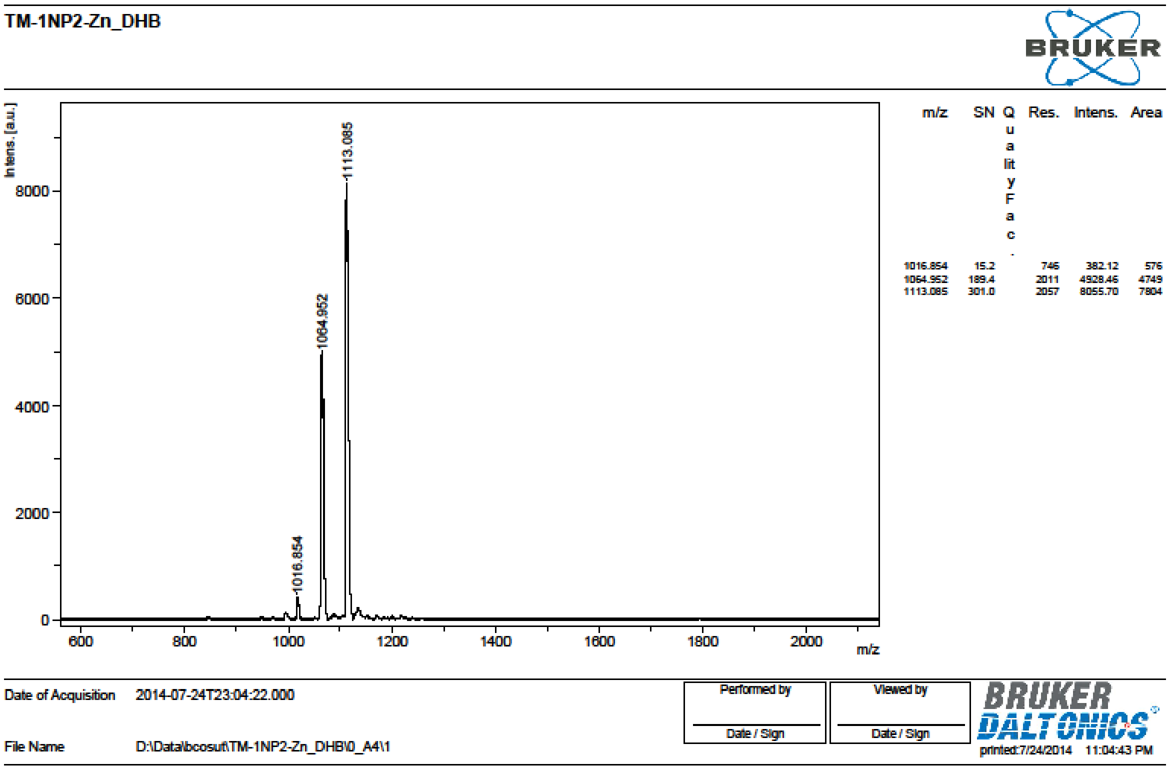
Date / Sign

Viewed by

Date / Sign

printed:7/24/2014 11:16:56 PM

Fig. S2. Positive ion in reflectron mode MALDI-TOF mass spectrum of compound **4** were obtained in 2,5-dihydroxybenzoicacid.



TM-1NP2-Zn_DHB

m/z	SN	QualityFac.	Res.	Intens.	Area
1016.854	15.2		746	382.12	576
1064.952	189.4		2011	4928.46	4749
1113.085	301.0		2057	8055.70	7804

Date of Acquisition 2014-07-24T23:04:22.000

File Name D:\Data\bcosut\TM-1NP2-Zn_DHB\0_A4\1

Performed by

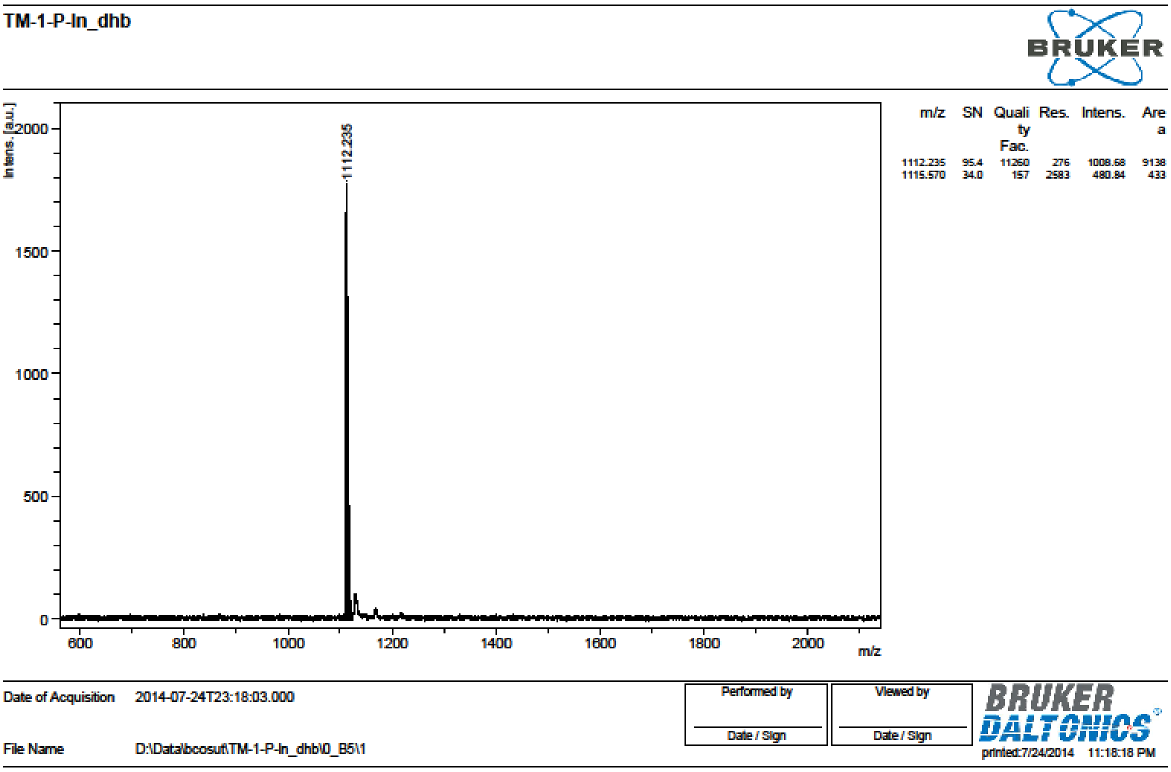
Date / Sign

Viewed by

Date / Sign

printed:7/24/2014 11:04:43 PM

Fig. S3. Positive ion in reflectron mode MALDI-TOF mass spectrum of compound **5** were obtained in 2,5-dihydroxybenzoicacid.



TM-1-P-In_dhb

m/z	SN	Quality Fac.	Res.	Intens.	Area
1112.235	95.4	11260	276	1008.68	9138
1115.570	34.0	157	2583	480.84	433

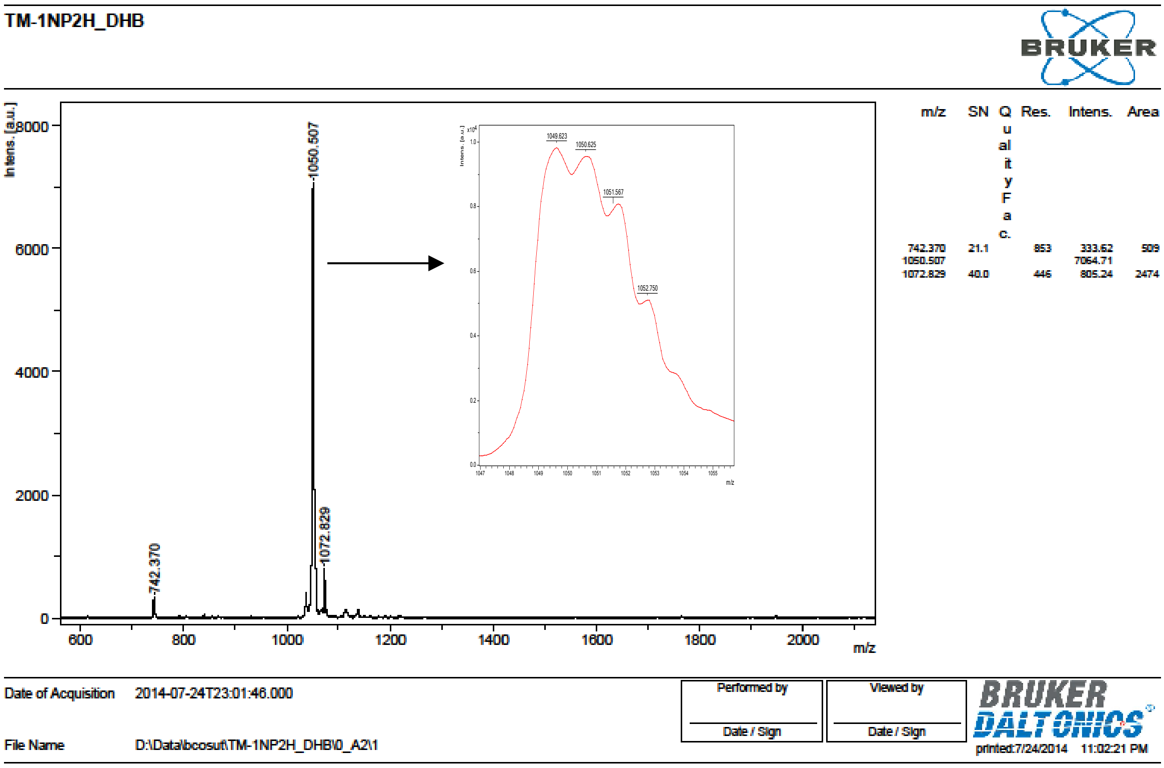
Date of Acquisition 2014-07-24T23:18:03.000

File Name D:\Data\bcosut\TM-1-P-In_dhb\0_B5\1

Performed by	Viewed by
Date / Sign	Date / Sign

printed:7/24/2014 11:18:18 PM

Fig. S4. Positive ion in reflectron mode MALDI-TOF mass spectrum of compound **6** were obtained in 2,5-dihydroxybenzoicacid.



TM-1NP2H_DHB

m/z	SN	Quality Fac.	Res.	Intens.	Area
742.370	21.1		853	333.62	509
1050.507				7064.71	
1072.829	40.0		446	805.24	2474

Date of Acquisition 2014-07-24T23:01:46.000

File Name D:\Data\bcosut\TM-1NP2H_DHB\0_A2\1

Performed by

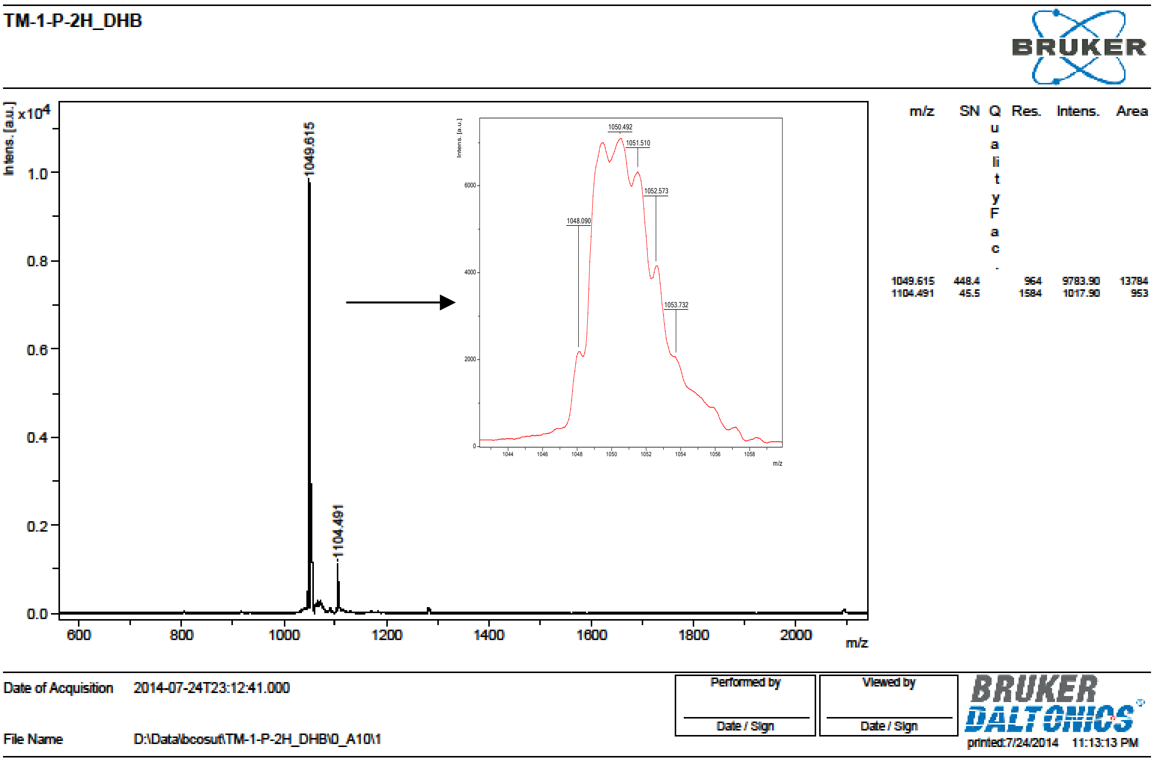
Date / Sign

Viewed by

Date / Sign

printed:7/24/2014 11:02:21 PM

Fig. S5. Positive ion in reflectron mode MALDI-TOF mass spectrum of compound **7** were obtained in 2,5-dihydroxybenzoicacid.



TM-1-P-2H_DHB

m/z	SN	Quality Fac.	Res.	Intens.	Area
1049.615	448.4		964	9783.90	13784
1104.491	45.5		1584	1017.90	953

Date of Acquisition 2014-07-24T23:12:41.000

File Name D:\Data\bcosut\TM-1-P-2H_DHB\0_A10\1

Performed by

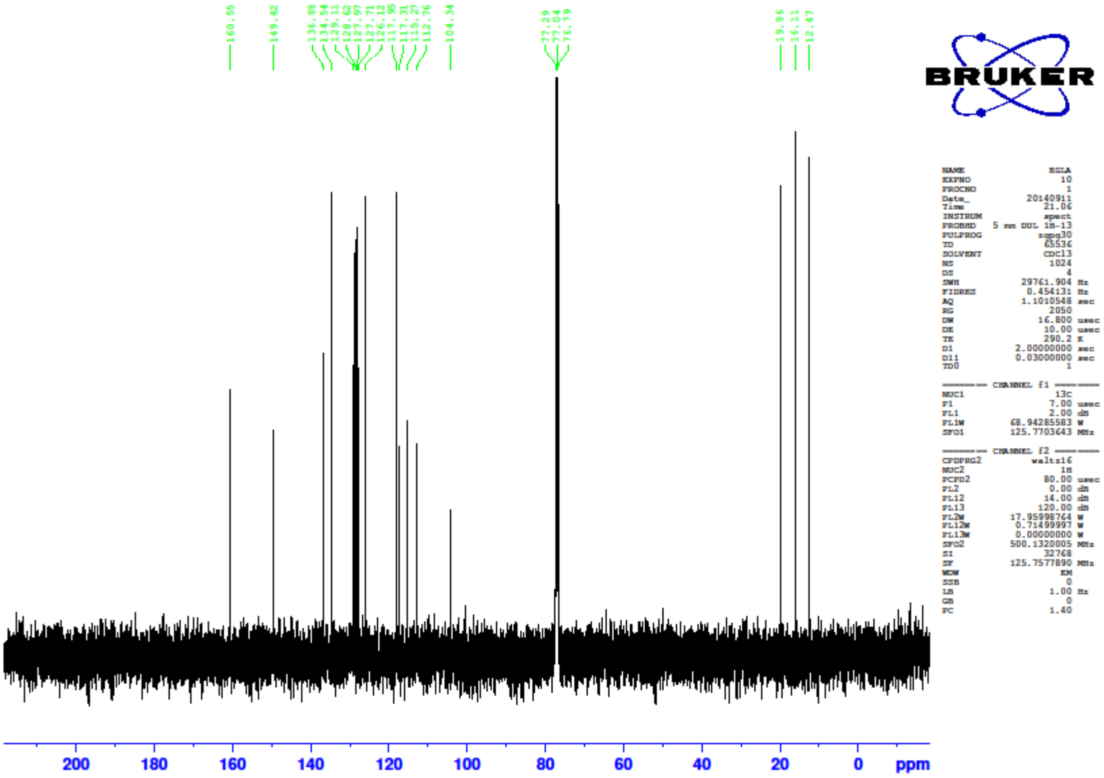
Date / Sign

Viewed by

Date / Sign

printed:7/24/2014 11:13:13 PM

Fig. S6. Positive ion in reflectron mode MALDI-TOF mass spectrum of compound **8** were obtained in 2,5-dihydroxybenzoicacid.



```
NAME                 EGLA
EXPNO                  10
PROCNO                  1
Date_            20140911
Time                21.06
INSTRUM             spect
PROBHD   5 mm DUL 1H-13
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010548 sec
RG                   2050
DW                 16.800 usec
DE                  10.00 usec
TE                  290.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.00 usec
PL1                  2.00 dB
PL1W          68.94285583 W
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                14.00 dB
PL13               120.00 dB
PL2W          17.95998764 W
PL12W          0.71499997 W
PL13W          0.00000000 W
SFO2          500.1320005 MHz
SI                  32768
SF            125.7577890 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Fig. S7A. ^{13}C-NMR spectrum of Compound **1**.

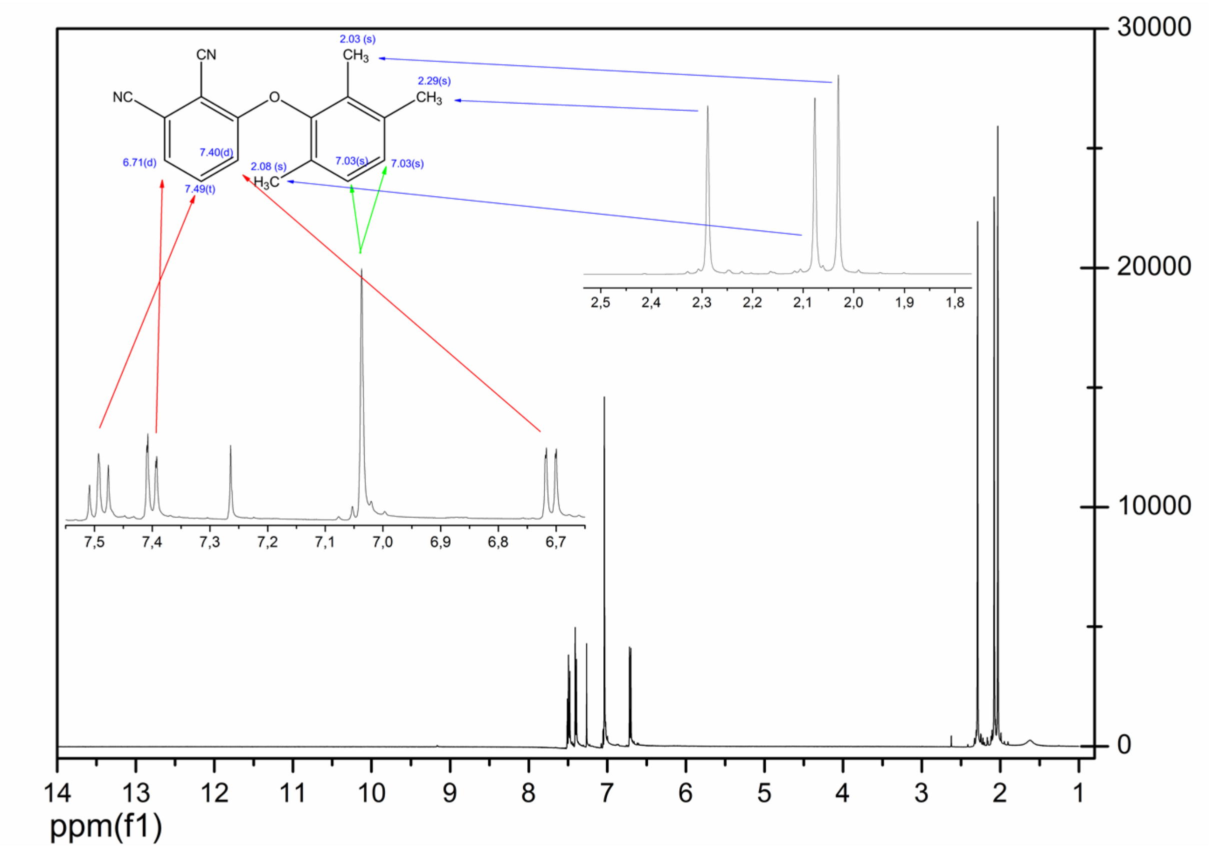


Fig. S7B. ^{1}H-NMR spectrum of Compound **1**.

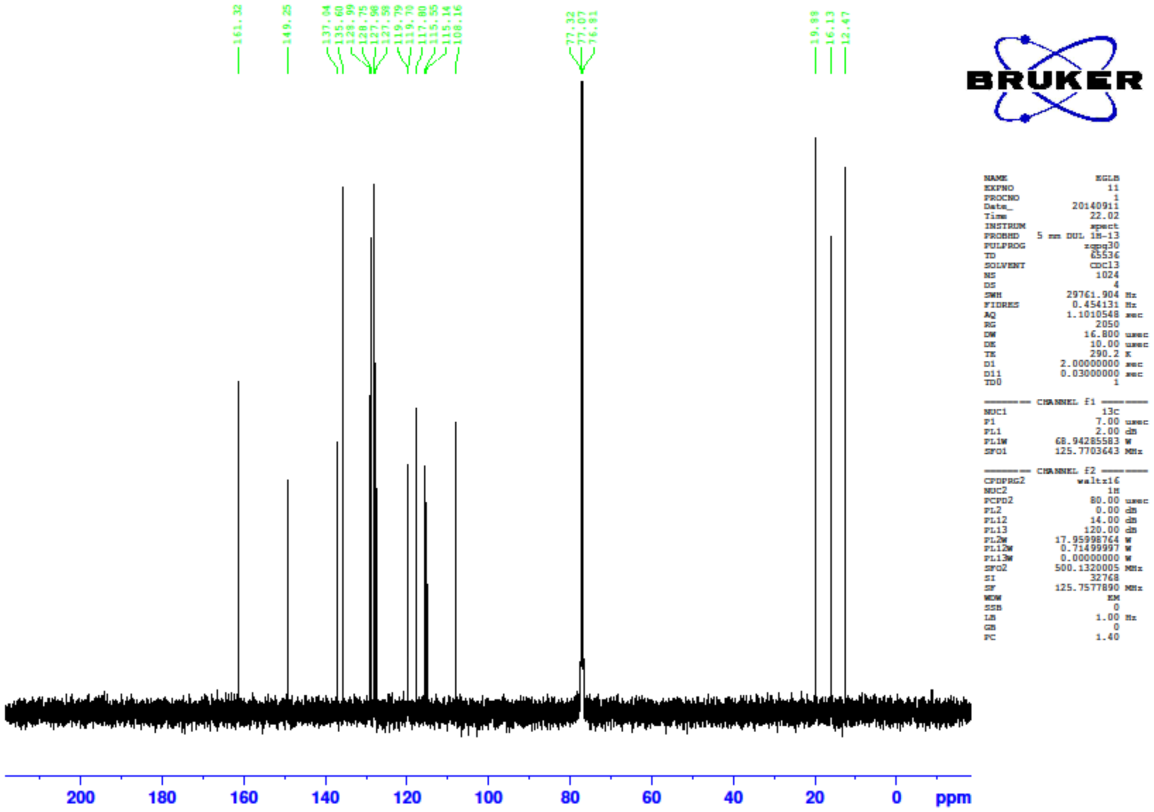


Fig. S8A. ^{13}C-NMR spectrum of Compound **2**.

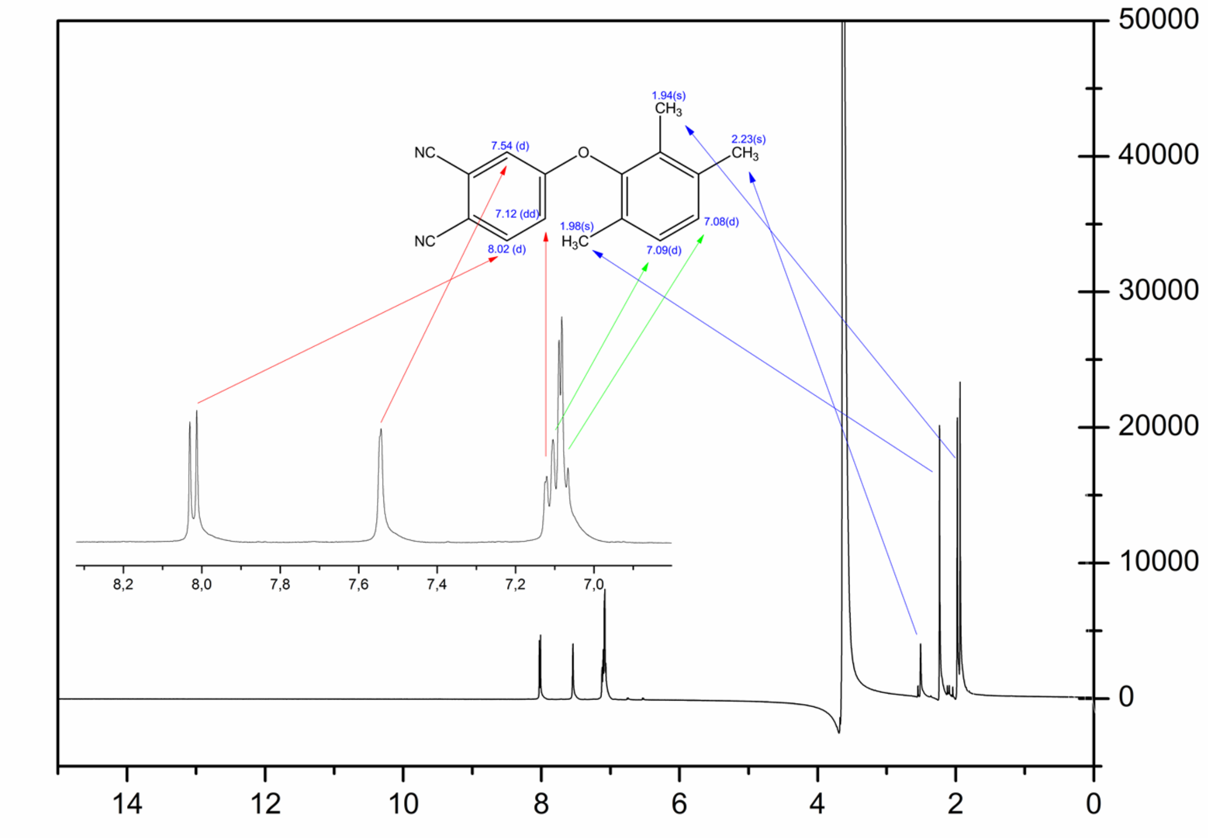


Fig. S8B. ^{1}H-NMR spectrum of Compound **2**.

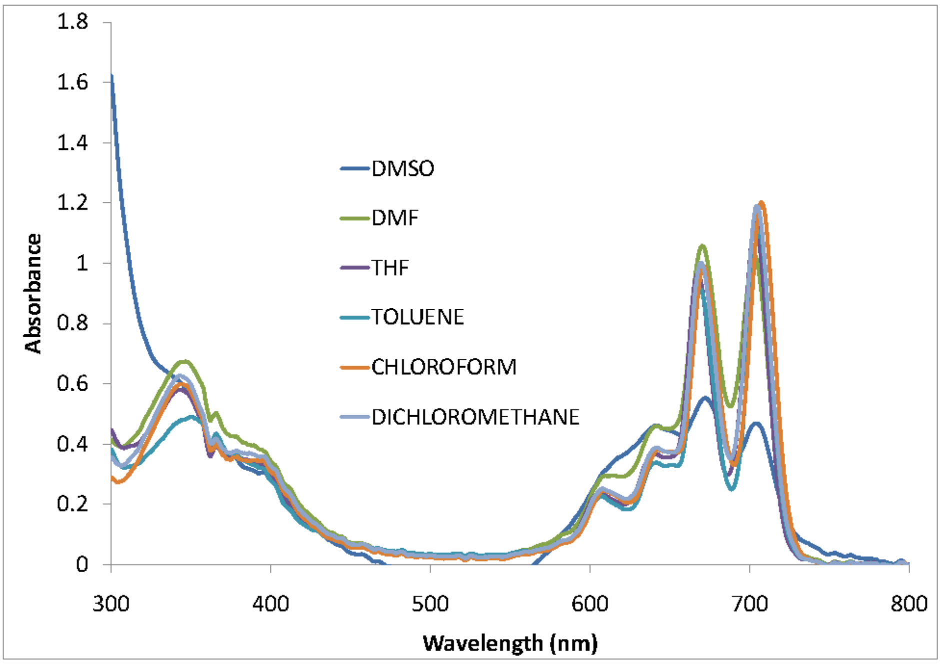


Fig. S9. Absorption spectra of complex **8** in different solvents.

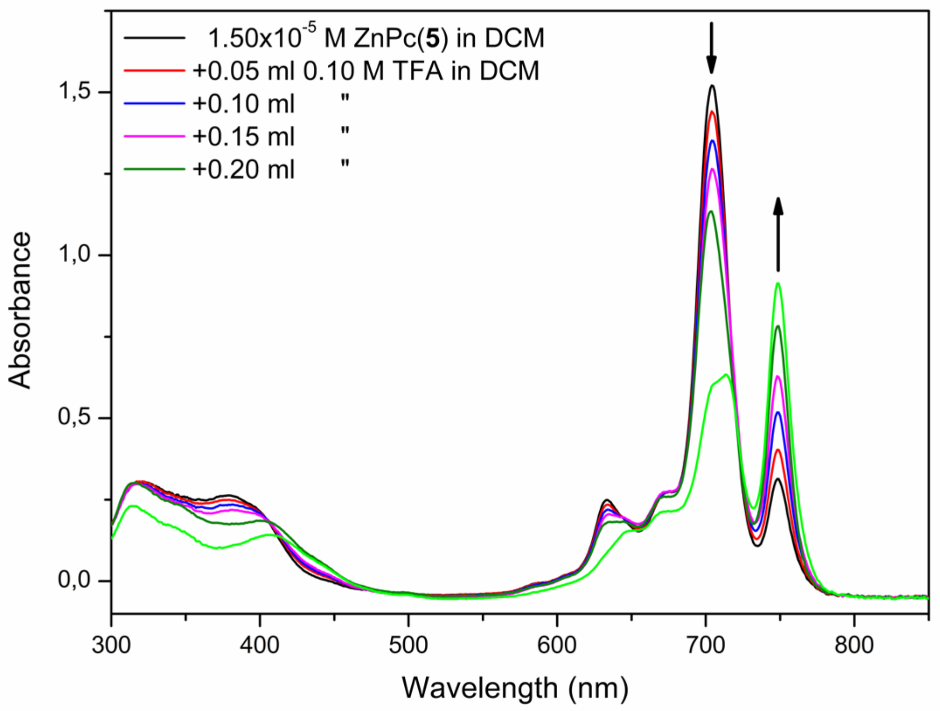


Fig. S10. UV–*vis* spectral changes of **5** in DCM by addition of TFA solution

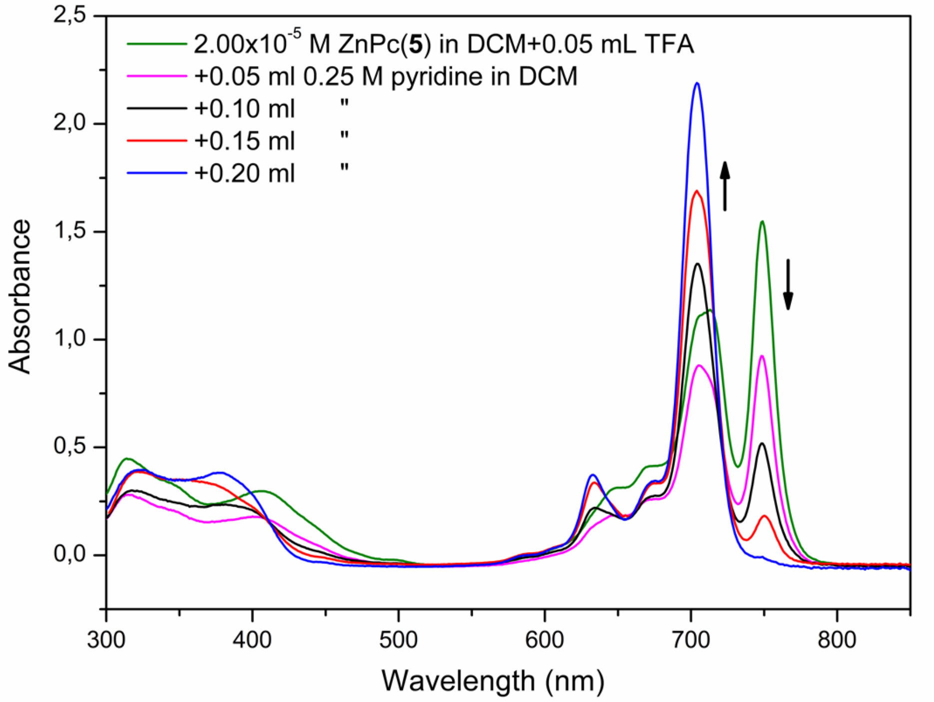


Fig. S11. UV–*vis* spectral changes of **5** in DCM and TFA by addition of pyridine solution.

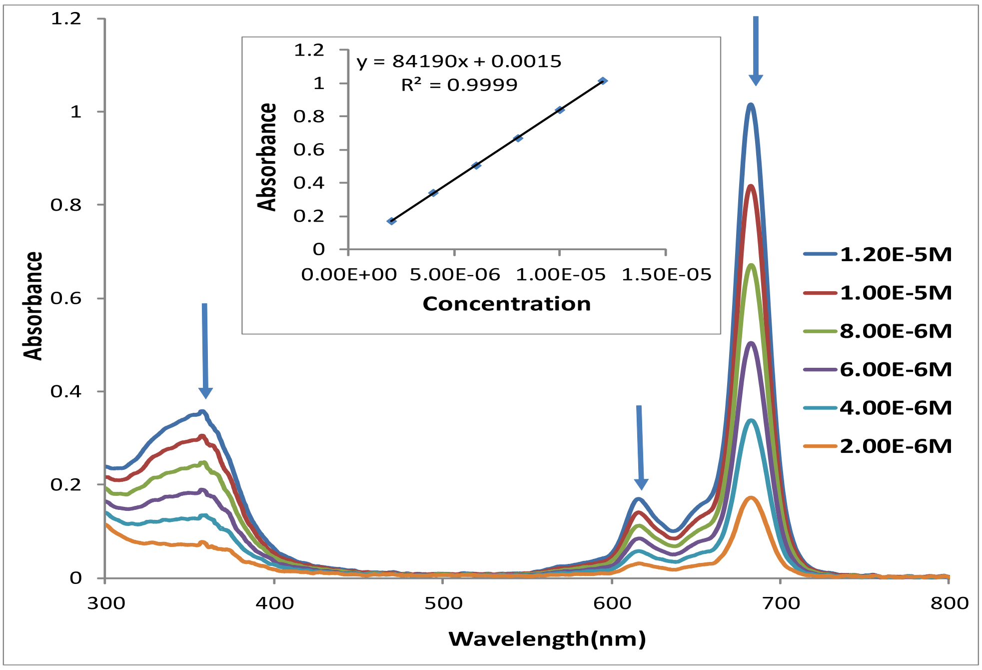


Fig. S12. Aggregation behavior of unsubstituted imdium acetate Pc (**InAcPc**) in DMF at different concentrations. (Inset: plot of absorbance vs. concentration.)

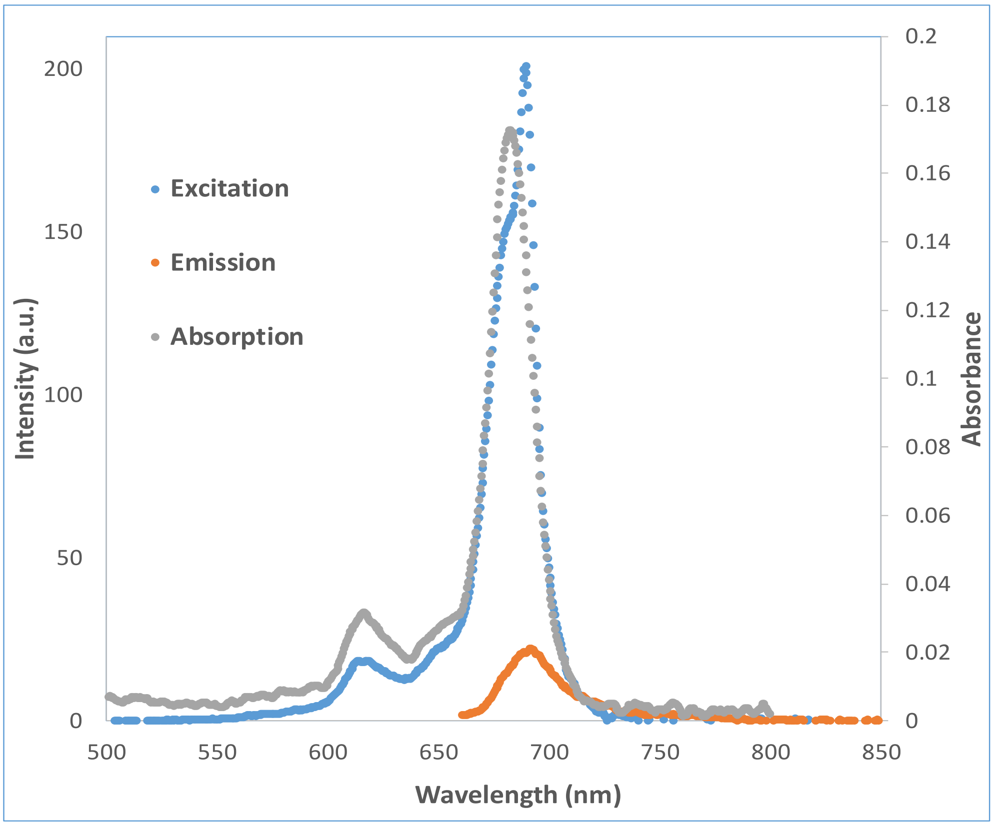


Fig. S13. Absorption, excitation and emission spectra of unsubstituted indium(III) acetate Pc (**InAcPc**) in DMF. Excitation wavelength = 651 nm

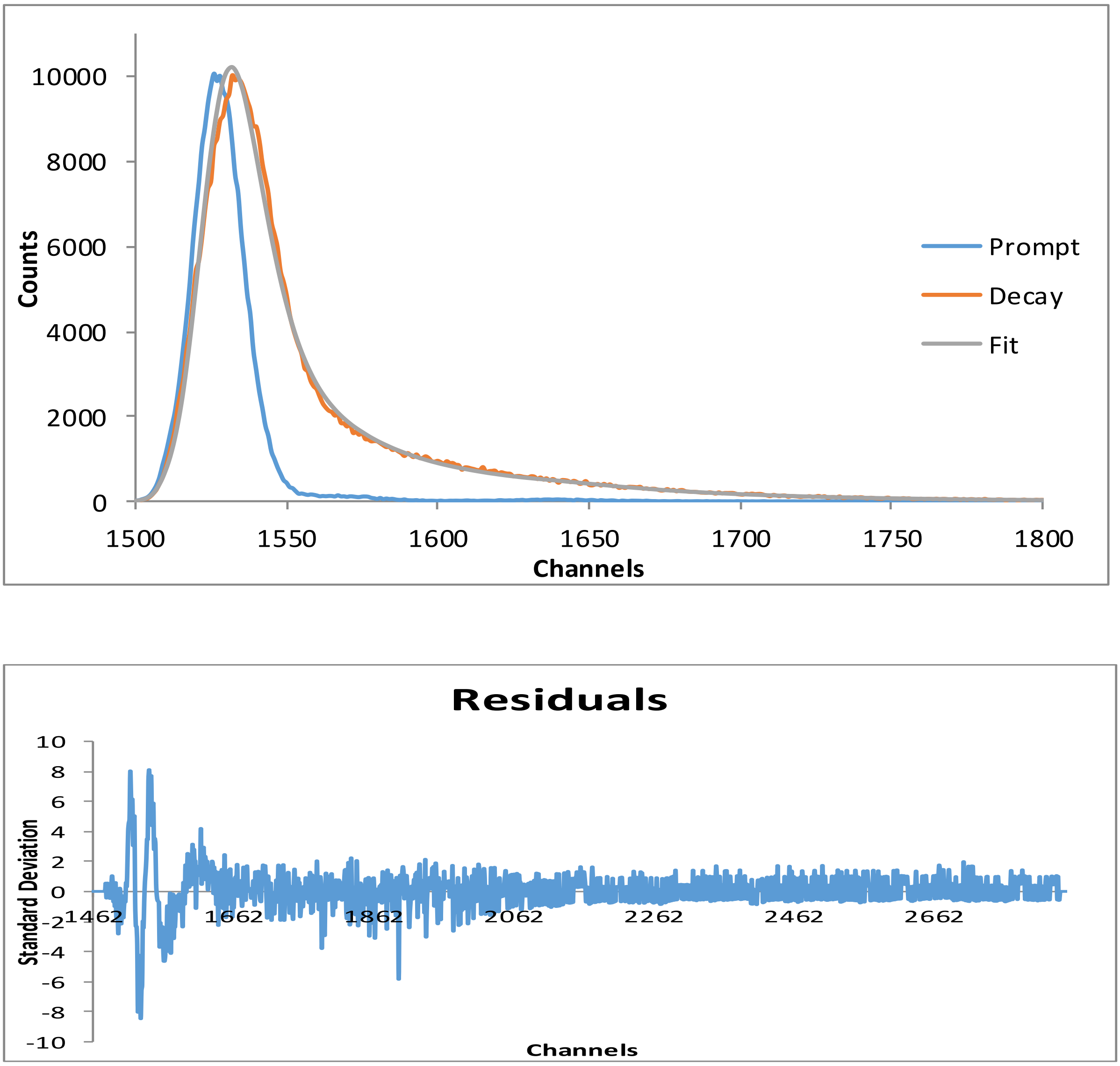


Fig. S14. Time correlated single photon counting (TCSPC) trace for unsubstituted In(OAc)Pc in DMF with residuals. Excitation wavelength = 651nm.

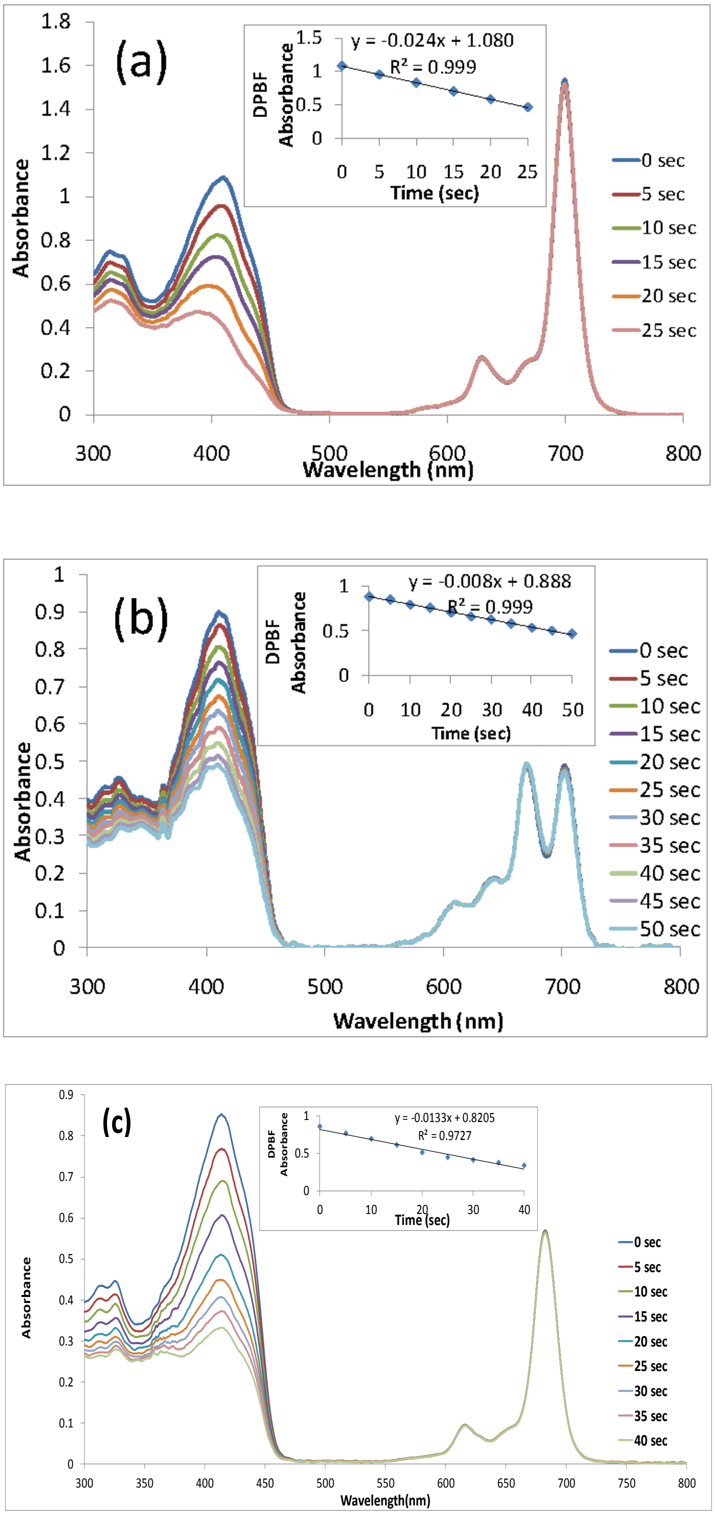


Fig. S15. A typical spectrum for the determination of singlet oxygen quantum yield of studied (a) zinc(II) in Pc (**5**), (b) metal free Pc (**8**) and (c) unsubstituted indium(III) acetate Pc (**InAcPc**) in DMF Concentration = 1×10^{-5} M (inset: plots of DPBF absorbance versus time)

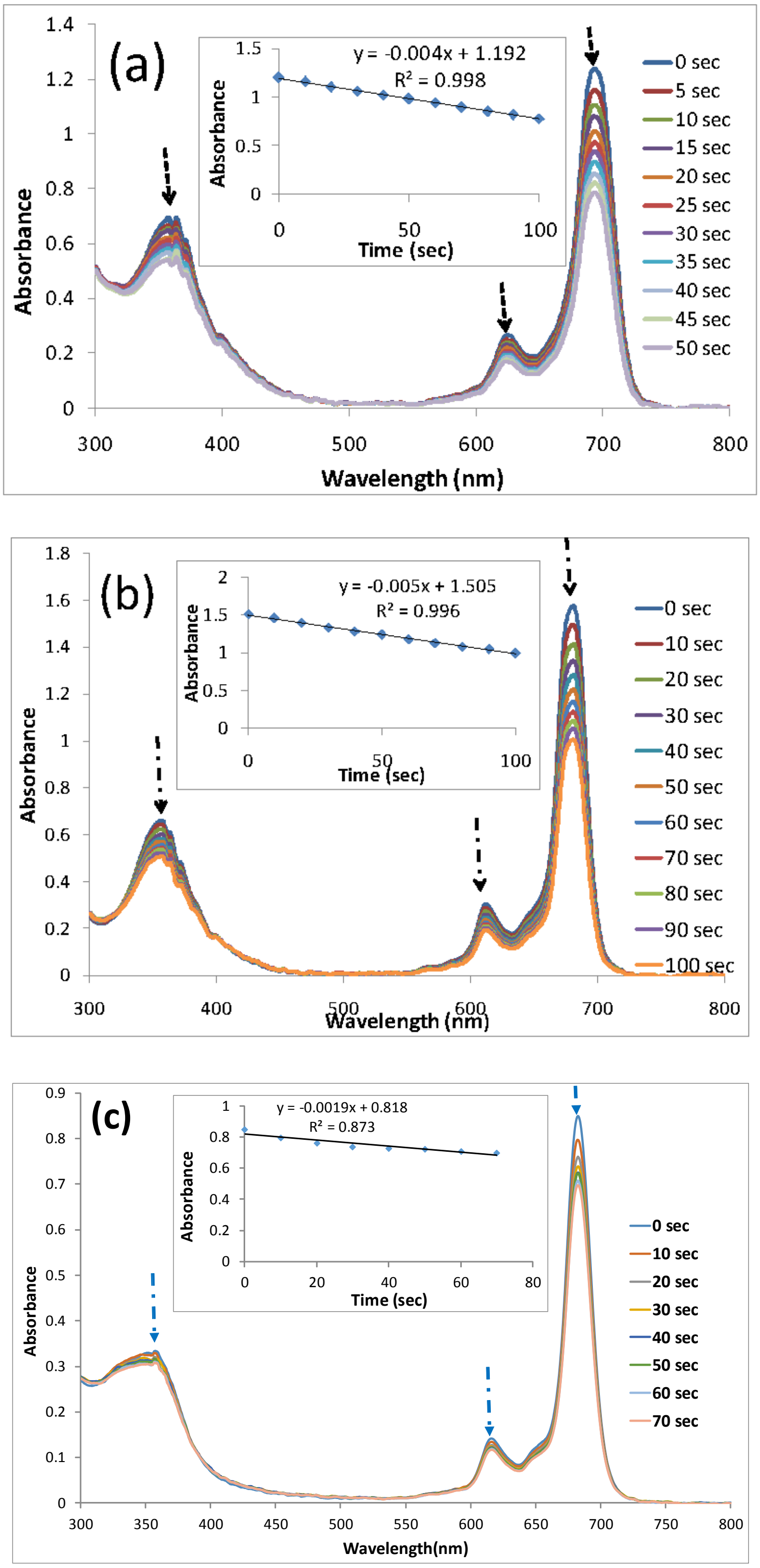


Fig. S16. The photodegradation of (a) studied indium(III) Pc (**4**), (b) studied zinc(II) Pc (**6**) and (c) studied unsubstituted indium(III) acetate Pc (**InAcPc**) in DMF (inset: plot of Q band absorbance versus time).

Table S1. The specific IR bands of the compounds (**1-8**)

The compounds	N–H stretch.	=C–H stretch.	$>CH_2$ stretch.	C≡N stretch.	C=O stretch.	C=N stretch.	C=C stretch.	C–H bend.	C–O stretch.	C–N stretch.	C–C stretch.
Ligand (**1**)	–	3088 3031	2946 2925 2861	2231	–	–	1585 1572	1494 1451	1325 1273	–	1078 1004
Ligand (**2**)	–	3078	2925 2861	2229	–	–	1596 1563	1483 1462	1321 1279	–	1068 1038
Unsubst. In(OAc)Pc	–	3048 3058 3023	2926 2860 2820	–	1722	1651	1606 1548	1474 1401	1330 1283	1160 1115	1080 1059
In(OAc)Pc (**3**)	–	3068 3023	2920 2856	–	1731	1672	1603 1585	1480 1410	1327 1248	1161 1119	1075 1002
In(OAc)Pc (**4**)	–	3058 3013	2922 2856	–	1734	1649 1676	1609 1573	1477 1462	1335 1267	1183 1116	1086 1042
ZnPc (**5**)	–	3058 3023	2922 2856	–	–	1657	1589 1570	1481 1456	1333 1267	1168 1118	1078 1001
ZnPc (**6**)	–	3058 3018	2921 2856	–	–	1656	1608 1575	1484 1460	1336 1267	1166 1117	1090 996
2HPc (**7**)	3292	3058 3023	2921 2851	–	–	1683	1595 1575	1486 1410	1333 1248	1155 1110	1077 1019
2HPc (**8**)	3290	3012	2983 2916 2854	–	–	1684	1614 1579	1462 1423	1318 1262	1160 1112	1076 1007