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Effects of O-substitution on the photophysical properties in solution and solid-state of BODIPY Dyes

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***Abstract*---**Crystal form emissive dyes play a key role in developing optical systems. In this work, we developed O-Bodipy fluorophores and studied their photophysical properties in solution and crystal form. We found that O-functionalization of the parent F-Bodipy could change the fluorescence efficacy in solution but it has very slight effect on the absorption and emission energies. The newly synthesized fluorescent compounds show intensive solid-state emission in the range (550-850 nm) with moderate quantum yield. The luminescent complexes with solid-state emission were anticipated to get wider usages for developing various fluorescent dyes with excellent optical properties for solid-state Laser, especially with the advantages of simple structure and easy synthetic route.

***Keywords*---**photophysical properties, solution solid-state, crystal**.**

Introduction

Bodipy and Aza-Bodipy are famous fluorescent dyes for their unique photophysical properties.[1,2] They have been used widely for detection of heavy metal ions[3,4], monitoring of enzymes [5,6] ,carbon monoxide releasing probe[7], light induced antimicrobial agents[8] , study protein surface hydrophobicity[9], photocages for light activated release[10] and for cellular dynamics [11] and living cell imaging[12]. In addition to the wide application of BODIPY in florescence area, more recently it has been reported that BODIPY could work as electron withdrawing group for asymmetric cycloaddition reactions. [13]

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Bodipy could be post modified easily by implementation widespread range of chemical reactions and synthetic procedures even sometimes regioselictivly to install diversity of functional groups at specific positions on Bodipy core.[14,15,16,17,18] Moreover, Bodipy can undergo nucleophilic substitution at the boron centre, B-F bond could be activated with different variety of Lewis acids including BF3,19 BCl3,20,21 BBr3,[22] AlCl3,[23,24] Et2AlCl [25] and SnCl4[26] in inert atmosphere followed by adding the suitable nucleophile which in turn could be internal nucleophile (intarmolecular attack) or external, the external nucleophile might be proton nucleophile (Nu-H) or trimethylsilyl nucleophile[27] (TMS-Nu). Furthermore, the modifications that take place on the boron atom keeps the special photophysical properties intact but improving the permanence and solvation with polar solvents or in carbon-based solvents. On other hand, O-Bodipy are stable compounds due to the fact that B-O bonds amongst the strongest element-element single bonds. O-BODIPY have been used for two main purposes either as energy harvesters [28,29,30,31,32] or as circularly polarized light emitters.[33,34,35,36,37,38]

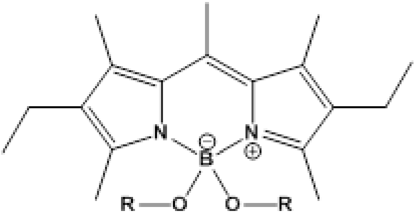
However, in condensed phases, Φf is considerably declined then the emission band is shifted to longer wavelengths owing to π-π stacking and reabsorption of luminescence predicated on the flat conjugated core and a minor Stokes shift, BODIPY typically set firmly in the solid form. The aforementioned giving rise to robust intermolecular contacts, inducing substantial emission efficacy reducing. Since the slight fluorescence quantum proficiencies in the dense phase, BODIPY pigments aren't appropriate to be utilized in uses like solid emitters. In order to tackle this lack, various research groups have applied the approach of connecting large substitute groups at different positions which include meso position and/or 2,6-positions and/or 3,5-positions to reinforce hindrance among neighboring molecules and avoiding aggregations.[39] This tactic is remarkably efficacious in refining the performance of BODIPY dyes as solid emitters. For instance Bulky triphenylsilylphenyl substituted BODIPY at the 2-position exhibits a relatively high quantum yield to 0.25 in powder form,[40] meso-trimethylsilylphenyl substituted Bodipy showed 0.045 in single crystal [41], substitution of triphenylamine instead of trimethylsilylphenyl on the same Bodipy platform enhances solid state quantum yield up to 0.19 in single crystal form[42] while substitution of mesityl group gave the highest quantum yield reported to date 0.32 in crystal state [43], However, due to the fact that luminescence of Bodipy initiates from the Bodipy core, large size substitute at the meso position frequently lead to a noteworthy effect on the emission wavelengths. In addition, substitution at the boron atom can enhance solid-state emission dramatically, For example, Φf in the solid state is 0.01 in common F-Bodipy. Instead, Φf changes to 0.25 or 0.30 by replacing two fluorine atoms by phenyl groups in different Bodipy platforms.[44,45] However the substitution that occur on boron atom can reserve absorption and emission energies. In our research group, we have tried to solve this problem by substitution of catechol group at the boron atom, unfortunately we found that catechol substituted Bodipy barely fluoresce in both solution and solid state.[46]

Herein, we introduced two crystal form emissive O-Bodipy, these dyes have been fabricated via linking each of 4-bromophenol and 4-tritylphenol with 4,4-Difluoro-1,3,5,7,8-pentamethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene to yield BODIPY-1 and BODIPY-2 individually. In the meantime, replacement of fluorine with oxygen at the boron atom could boost the chemical stability of the produced dyes and enhance the quantum yield via quenching the intermolecular stacking; it's worth to do develop such kind of dyes for its potential application in optoelectronic devices.

Results and Discussion

Synthesis and crystal structures

Total syntheses of BODIPY-1 and BODIPY-2 were accomplished by substitution two fluorine atoms of (4,4-Difluoro-1,3,5,7,8-pentamethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene) with the corresponding phenol. This compound has smoothly functionalized in this project via straight knitting of two phenol derivatives (4-bromophenol) and (4-tritylphenol) to give BODIPY-1 and BODIPY-2 respectively with moderate yield. ^{11}B-NMR showed singlet signal in upfield because boron atom is shielded and no ^{19}F-NMR signal has detected.



BODIPY-1 R= 4-BrPh
BODIPY-2 R= 4-TritylPh

Scheme-1 chemical structures of BODIPY-1 and BODIPY-2

Suitable crystals for X-ray diffraction analysis were obtained for BODIPY-1 by slow evaporating of Ethyl acetate-Hexane solution in room temperature. In spite of the amorphous nature of tetraphenylmethane group,[47,48] we managed to get crystals of BODIPY-2 by slow diffusion of ether in dichloromethane solution, thanks to O-BODIPY for its ability to be crystallisable. The structure of the two compounds is presented in (Fig 2 and 3). BODIPY-1 and BODIPY-2 gave monoclinic forms with C2/c and P21/c space groups respectively.

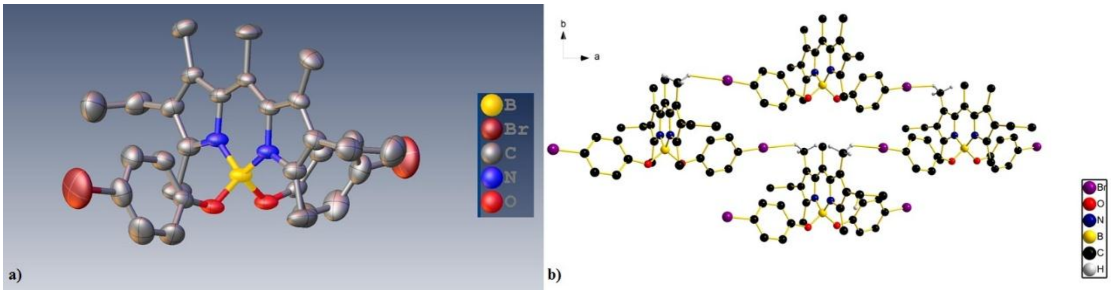


Figure-1 a) olex2 view [49] shows the crystal structure of BODIPY-1, Hydrogen atoms absent for clearness, b) packing of molecules in a unit cell, hydrogen atoms omitted for clarity except few hydrogen atoms to show the intermolecular hydrogen bonding

X-ray crystallography revealed that BODIPY-1 is a symmetrical molecule with C2 element of symmetry in which the two B-O bonds equal to each other and the two B-N bonds equal to each other too. On other hand, BODIPY-2 non-symmetrical molecule, interestingly we noticed that the two ethyl groups at position 3 and 5 appointing to the same direction so the molecule could be chiral molecule and BODIPY-2 compound could be racemic mixture. In both compounds, boron is in a distorted tetrahedron geometry. The angles around the boron atom are slightly deviated than 109.5°. As shown in Table-1.

Table-1 some selected bond distances and angels

Bond (A) Angles (deg)	B-O1 B-O2	B-N1 B-N2	O1-B-O2	N1-B-N2	O1-B-N1 O1-B-N2 O2-B-N1 O2-B-N2
BODIPY-1	1.453 1.453	1.543 1.543	101.2	105.6	111.50 113.64 111.50 113.64
BODIPY-2	1.450 1.456	1.560 1.548	103.7	105.4	110.2 113.2 113.4 111.1

BODIPY-1 molecules pack in unit cell as parallel zigzag up and down (down left – up right –down left). Bromine atoms play a crucial role of molecular packing; they form net of hydrogen bonding helps molecules to arrange in parallel form. The bromine atom of one molecule form hydrogen bond with the hydrogen atom of methyl group attached to carbon number one of BODIPY-1 core of neighbouring molecule while the other bromine atom form hydrogen bond with the methyl hydrogen attached to carbon number seven of another neighbouring molecule. The measured distance between the bromine and the hydrogen atom around 2.796 A which is in the range of the hydrogen bonding reported before.[50] The centre-to-centre distances between the boron atoms are the same in all direction and equal to 11 A and the molecules are distributed regularly in the crystal lattice, such great distance between two adjacent molecules indicating that there is almost no π-π stacking between the neighbouring dimers owing to the bulky aromatic moieties. Four molecules of BODIPY-2 are present per unit cell; the molecules are packed in antiparallel pattern with shortest contact being 3.7 A between the methyl carbon attached at position 1 on BODIPY core and the meta carbon of phenyl group attached to the oxygen. The centre-to-centre distances between the boron atoms between two neighbouring molecules in average 10 A. We did not notice any effective π-π stacking.

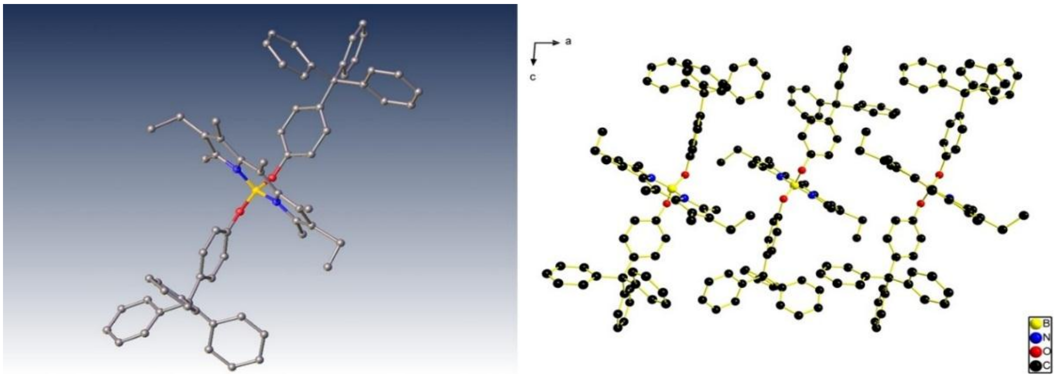


Figure-2 this shows olex2 view of the crystal structure of BODIPY-2 and packing of molecules in a unit cell Hydrogen atoms omitted for clarity.

Photophysical properties in solution

In order to consider the potential value of BODIPY-1 and BODIPY-2 as suitable fluorescent pigments, the optical properties were evaluated for both probes .We noticed analogous styles of absorbance and fluorescence for BODIPY-1 and BODIPY-2 (Fig-3 and table-2). BODIPY-1 displayed maximum absorption at (520-526 nm) in numerous solvents, the molar extinction coefficient was determined in ethanol and found to be equal to 74600 cm^{-1} M^{-1} while BODIPY-2 exhibits maximum absorption at 520-527 nm, BODIPY-2 shown lower molar extinction coefficient than BODIPY-1 which equal to 52200 cm^{-1} M^{-1} in ethanol.

Table-2 Photophysical properties of BODIPY-1 and BODIPY-2 in ethanol

Comp.	λ_{abs}	λ_{em}	Є	Φ_f
BODIPY-1	520 nm	548 nm	74600 cm^{-1} M^{-1}	0.93
BODIPY-2	520 nm	541 nm	52200 cm^{-1} M^{-1}	0.66

BODIPY-1 and BODIPY-2 exposed fluorescence peaks maxima at 541-552 nm in numerous solvent, the fluorescence intensities were greater in carbon-based solvents than related ones measured in water. Both compound exposed very small stock shift 21-28 nm. It is obvious that o-functionalization of the parent F-BODIPY slightly affects the absorption and emission peaks (F-BODIPY λ_{ab} 517 and λem 546 in ethanol)[51]; however, BODIPY-1 provided high florescence quantum yield value (Φf 0.93 in ethanol) more than what reported for F-BODIPY (Φf 0.7 in ethanol)[51] while substitution of the fluorine atoms with 4-trytlyphenol reduced the quantum yield to 0.66 and this could be attributed to the rotation of eight phenyl groups that can afford non-radiative pathway to the ground state.

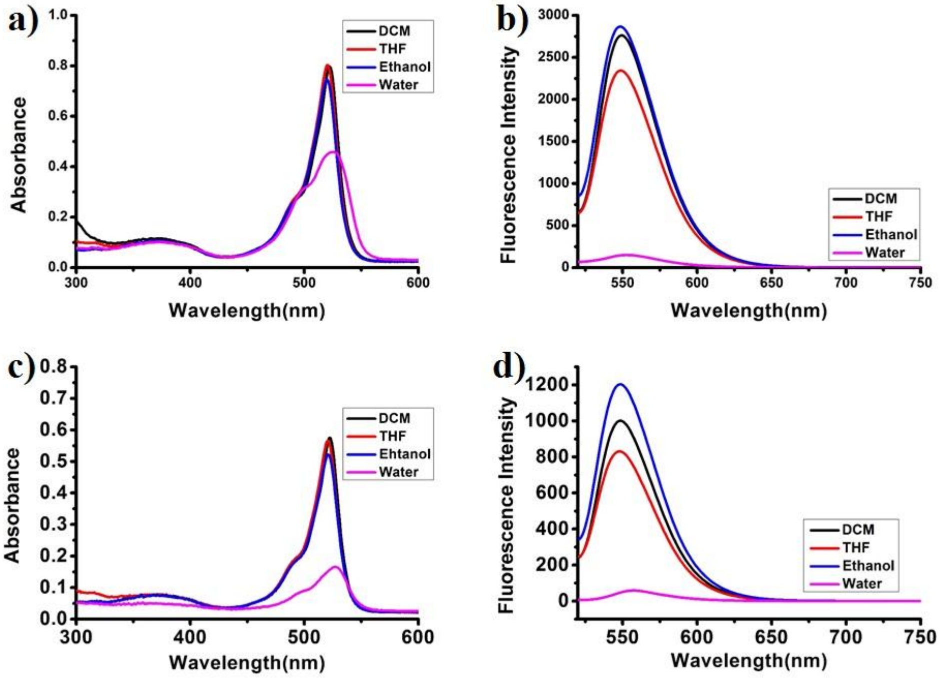


Fig. 3 a) absorption spectra and b) emission spectra of BODIPY-1 different solvents, c) absorption spectra and d) emission spectra of BODIPY-2 in series of solvents. λ_{ex} 510 nm, λ_{em} 520–750 nm, 10 μM. slit width 2nm and PMT voltages 700 v

Crystal form photophysical properties in

So as to examine the crystal form photophysical properties for BODIPY-1 and BODIPY-2, we studied luminescence emission spectra, lifetime, excitation spectra, and calculated luminescence quantum yield (table-3). BODIPY-1 compound exhibited excitation at 432 nm of the radiation while BODIPY-2 showed excitation at 475 nm (fig. S-8). After excitation at the proper wavelength the corresponding fluorescence of both compounds take place between 550-850 nm, BODIPY-1 showed monomodal emission curve in the range 550-850 nm the peak is centred at 597nm while BODIPY-2 showed monomodal emission curve in the range 550-850 nm and the peak is centred at 584 nm. In previously research work, we found that F-BODIPY displays feeble emission maximum at 637 nm, this significant blue shift in the emission spectra of BODIPY-1 and BODIPY-2 comparing to parent platform could be attributed to quenching of the intermolecular stacking by the bulky groups.

Table-3 Photophysical properties of BODIPY-1 and BODIPY-2 in crystal solid state

Comp.	λ_{ex}	λ_{em}	Φf	T1	T2	K_f/s^{-1}	K_{nr}/s^{-1}
BODIP	432	597	2.8	1.263 ns	4.531 ns	9.8	3.3

Y-1	nm	nm	6%	(34.02%)	(65.98%)	x10^6	x10^8
BODIPY-2	475 nm	584 nm	5.63%	0.619 ns (80.18%)	1.384 ns (19.82 %)	5.6 x10^7	9.4 x10^8

Fluorescence lifetime has been measured for maximum emission peak; an exponential kinetic model was applied to fit the excited state relaxation. Both compounds displayed very small lifetime value (table-3), such short lifetime could be ascribed to the fast rotational relaxation to the ground state; the fluorescence quantum yield of BODIPY-1 lower than that of BODIPY-2 which showed moderate rate which could be recognized to the effect of quenching π-π staking via bulk substituents that act as spacers between the adjacent molecules.

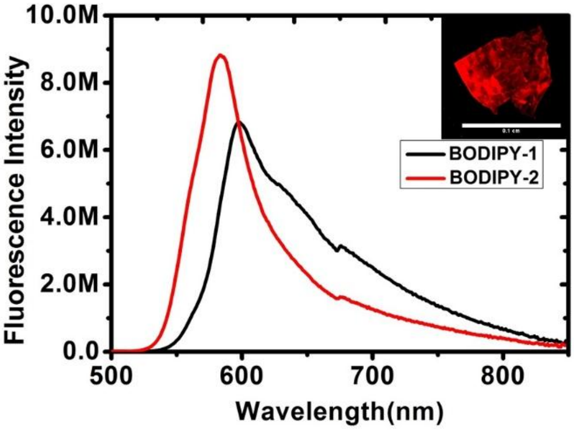


Fig-4 emission spectra of BODIPY-1 and BODIPY-2 in solid state, the inset is the crystal of BODIPY-1 under confocal fluorescent microscope

Conclusions

The aim of this project is to study the effect of O-substitution on crystal structure and optical properties of BODIPY; we prepared O-Bodipy substituted with 4-bromophenol and 4-tritylphenol to produce BODIPY-1 and BODIPY-2 respectively. The synthesized compounds have characterized unambiguously by HRMS, ^{1}H NMR ,^{13}C NMR and ^{11}B NMR. X-ray crystallography shown that BODIPY-1 and BODIPY-2 form monoclinic crystals with space group, C2/c and P21/c with low molecular interactions and long centre to centre distance between adjacent molecules. Both compounds BODIPY-1 and BODIPY-2 display strong solid-state luminescence with efficiency up to 5.63% (for BODIP-2) in the crystalline forms. This result may open a path to engineer original fluorescent emitters that have better photophysical intrinsic worth, we think that substitution at both meso and boron atom positions can push the quantum yield of Bodipy dyes in solid state to the edges.

Experimental

Chemical materials acquired from well-known chemical suppliers with high purity. Bruker Advance III 400 MHz was used for collecting ^{1}H NMR data, ^{13}C NMR (100 MHz) and for ^{11}B NMR (128 MHz), in deuterated chloroform (CDCl3), tetramethylsilane was used as standard). HRMS (high-resolution mass spectrometry) spectra has been done by Bruker Apex IV FTMS with negative electrospray ionization for BODIPY-1 and positive atmospheric pressure chemical ionization for BODIPY-2. Purkinje TU-1901 spectrophotometer was used for recording absorption spectra. Luminescence measurements and quantum yield counting in solution were reserved with Hitachi F-7000 spectrofluorometer using 1cm quartz cuvette. D8 Venture Advance diffractometer (Bruker Company) was used to perform the analysis related the absolute configuration via Single crystal XRD. Crystal images taken by fluorescent microscope (CLSM, FV1000 microscope).

Luminescent compounds Synthesis

- Preparation of F-BODIPY (4,4-Difluoro-1,3,5,7,8-pentamethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene) has been prepared and identified as described in literature .[51]
- Method for preparation of BODIPY-1 and BODIPY-2
  F-BODIPY (0.25 gm, 0.786 mmol, 1eq) was dissolved in anhydrous CH_2Cl_2 (30 mL) then stirred under nitrogen. $AlCl_3$ (0.526 gm, 3.93 mmol, 5eq) was transferred to the flask and the reaction mixture was tortured in room temperature till the colour of the solution has vanished converted to violet. The appropriate phenol derivative (3.93 mmol, 5eq) dissolved in tetrahydrofuran was added then stirring continued over 24h followed by rapid flushing through column packed with deactivated basic alumina (CH_2Cl_2 used as eluent). More purification was required to get the final product by silica column chromatography (petroleum ether / DCM 1/1).
  - 4.1.2.1 Preparation of BODIPY-1
    BODIPY-1 was prepared following the aforementioned method from 4-bromophenol. Red powder, Yield 51%, Rf 0.50 (Hex-AcOEt 4-1). 1H NMR (400 MHz, CDCl3) δ 7.01 (4 H, d, J 8.9), δ 6.26 (4 H, d, J 8.9), δ 2.60 (3 H, s), δ 2.36 (6 H, s), δ 2.28 (6 H, s), δ 2.22 (4 H, q, J 7.6), δ 0.86 (6 H, t, J 7.6). 13C NMR (101 MHz, CDCl3) δ 154.73, δ 151.61, δ 135.68, δ 131.35, δ 131.14, δ 130.85, δ 119.27, δ 116.40, δ 110.55, δ 16.09, δ 16.02, δ 13.81, δ 13.60, δ 11.64. 11B NMR (128 MHz, CDCl3) δ 0.57. MS: m/z calcd for [C30H32BBr2N2O2]-: 623.0929 [M-H]-; found: 623.0903, [M-H]-.
  - 4.1.2.2 Preparation of BODIPY-2
    BODIPY-2 was prepared following the aforementioned method from 4-Tritylphenol. Orange powder, Yield 33%, R_f 0.55 (Hex-AcOEt 4-1).^{1}H NMR (400 MHz, CDCl3) δ 7.07 (30 H, m), δ 6.67 (4 H, d, *J* 8.9), δ 6.29 (4 H, d, *J* 8.9), δ 2.50 (3 H, s), δ 2.37 (6 H, s), δ 2.30 – 2.08 (10 H, m), δ 0.81 (4 H, t, *J* 7.5).^{13}C NMR (101 MHz, CDCl3) δ 153.79, δ 151.49, δ 146.35, δ 146.07, δ 135.87, δ 130.49, , δ 130.11, , δ 126.11, δ

124.77, δ 124.58, δ 116.51, δ 113.79, δ 63.24, δ 63.17, δ 16.04, δ 15.93, δ 13.87, δ 13.52, δ 11.85.. ^{11}B NMR (128 MHz, CDCl3) δ 0.86. MS: m/z calcd for $[C_{68}H_{64}BN_2O_2\ ]^+$: 951.5063$[M+H]^+$; found: 951.5035, $[M+H]^+$.

Fluorescence and absorption spectra measurements

Standard solution with 1000 μM concentration of each fluorescent dye was prepared in dry DMSO, suitable volume of the Standard solution was transported into 10 cm3 volumetric flask; the volume completed by addition the required solvent to get 10 μM concentration of each compound dissolved in the required solvent. The spectra have been recorded in room temperature with 1cm quartz cell.

Solution luminescence Quantum yield measurements

Several solution with gradient concentration of Rhodamine 6G (Φ=95), BODIPY-1 and BODIPY-2 were prepared in ethyl alcohol, having different absorbance between 0.01-0.1 at the excitation wavelength 535 nm. The fluorescence area between 500 to 700 nm has been calculated for each sample. Plotting the fluorescence intensity area against the solution absorption value produced linear relationship then the slope has been calculated and used for computing the fluorescence quantum yield from the below equation.

$$\emptyset x = \emptyset R \left(\frac{mx}{m_R}\right)\left(\frac{n^2}{n_R^2}\right)$$

Where Φ quantum yield, x referring to sample, m is the slope from drawing the fluorescence area against the absorbance, the solvent refractive index is abbreviated as n, and R is referring to the reference.

Crystal form luminescence spectra and efficiency

FLS 980 spectrofluorometer Edinburgh Instruments Ltd., was used to record Crystal form fluorescence spectra, by loading appropriate amount of each sample (50 mg) in the sample holder and the fluorescence curve recorded after using the suitable excitation wavelength. Luminescence Quantum yield has been calculated by applying the integrated sphere technique. Radiative fluorescence according to the equation $Kf = \frac{\Phi}{\mathrm{T}}$, Non-radiative fluorescence according to the equation $Knr = (1 - \Phi)/\mathrm{T}$, average fluorescence lifetime has been used for calculation.

Conflicts of interest

There are no conflicts to declare

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