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Synthesis, Photophysics of a Novel Green Light Emitting 1,3,4oxadiazole and its application in FRET with ZnSe/ZnS QDs donor

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Abstract: The design and synthesis of a novel molecule 2-(4-((E)-2-(5-((E)-4-(5-(4-tertbutylphenyl)-1,3,4-oxadiazol-2-yl)styryl)thiophen-2-yl)vinyl)-5-(4-tert-butylphenyl)1,3,4oxadiazole (2TVPO) based on Donor- π -Acceptor strategy through the Wittig reaction as well as characterization by ¹H, ¹³C NMR spectroscopy, high resolution mass spectrometry and FT-IR spectroscopy forms the central theme of the present work. Thermal (TGA and DSC), photophysical and electrochemical properties have been studied in detail for this novel probe. In addition, fluorescence resonance energy transfer (FRET) employing steady state and time resolved spectroscopy methods has been studied using core-shell ZnSe/ZnS QDs (7 and 8 nm) and 2TVPO fluorescent probe, respectively, as the energy donor and acceptor. Results of these studies reveal that (i) FRET pairs show a strong dipole-dipole interaction tendency to transfer energy from donor to acceptor; (ii) they possess high FRET efficiency and (iii) strong dependence of the acceptor emission on the overlap integral, quantum dot size and donoracceptor distance. Further, the type of quenching is analyzed by Stern–Volmer plots.

Keywords: Wittig reaction, FRET, oxadiazole, Solvatochromism, ZnSe/ZnS QDs, Stern–Volmer plots.

1. Introduction

One of the important and intriguing aspects of modern nanotechnology is to develop new nanomaterials and systems, which can considerably enhance the effects of organic molecules traditionally applied in photosensitization [1-2], energy conversion [3], optoelectronics, etc. On the other hand, the synthesis, design and development of novel organic chromophores with efficient photophysical and optoelectronic properties have caught increasing attention because of their potential applications in organic light-emitting diodes (OLEDs), organic solid-state lasers, organic solid-state sensors and light-emitting electrochemical cells [4-8]. At present, the incorporation of donor group (D - electrondonating) and acceptor group (A - electron deficient) is the most appealed strategy in organic electronics field. In particular, π -conjugated donor-acceptor (D- π -A) fluorescent chromophores are very much useful in variety of applications [6-8] due to their efficient absorption/emission properties originated through intramolecular charge transfer (ICT) from D to A via π -bridge. Oxadiazoles being electron deficient are known for holeblocking/electron-transporting materials in OLEDs [9-10 and references therein] which restrict the π -conjugation to have deeply laying highest occupied molecular orbitals (HOMOs) along with high triplet energies [11-13]. Such promising class oxadiazoles are also being used in various biological activities [14].

In the last couple of decades, semiconductor nanocrystals and their applications have dramatically diverted science in the direction of new world due to their unique and remarkable optical, electrical, chemical and mechanical properties. Such nanostructures have found potential applications in the fields of luminescence tagging, biomedical applications like drug delivery, biological imaging, diagnostics and therapeutic purposes, multiplexing and recently biosensing [15-18]. Specifically, core/shell nanocrystals are interesting, in that, they exhibit enhanced fluorescence intensity and increased photostability. Over the past decade, extensive experimental work has been carried out on the synthesis of core/shell nanostructures, with tailored properties [19-21] that include CdSe/ZnSe, CdSe/CdS, CdSe/ZnS, CdS/HgS, ZnS/CdS, ZnSe/ZnS, HgS/CdS, CdS/PbS, etc., [22-28] which show reduced lifetimes, enhanced quantum yields and advantages in the tuning of relative bandgaps between the core and shell materials. Zinc Selenide (ZnSe) an interesting n-type, II-VI class, direct bandgap semiconductor has caught great attention owing to its key applications in photodetectors, full color displays and light emitting diodes (LEDs) [29-30]. Variety of core-shell nanocrystals have been synthesized with ZnS as an inorganic

passivation shell because of its wide bandgap (2.7 eV in bulk) and considerably large binding energy (i.e., 21 meV) [31] with a view to improve the emission properties and stability of core nanocrystals while acting as a protective layer to reduce the toxicity of core materials such as CdS. Norris et. al. have reported that ZnSe acts as an attractive host in formation of the doped nanocrystals [32]. Further, there is a good match between ZnSe and ZnS as it gives high photoluminescence (PL) efficiency and high chemical stability. The PL is trapped in the ZnSe core quantum dot (QD) when ZnSe and ZnS form core/shell structures. The core/shell ZnSe/ZnS QD structures have high luminescence efficiencies, less surface defect states and less toxicity in their variety of applications [22-28,33-34]. Therefore it is imperative to know the mechanisms of interaction between ZnSe/ZnS QDs and other chromophores.

Semiconductor quantum dots have been increasingly employed in the study of fluorescence resonance energy transfer (FRET) due to its ample applications in light harvesting in photosynthesis, biolabeling, structure determination and multiplexing experiments, design of sensors [35-38], etc,. Earlier reports [1,34,39] have demonstrated the possibility of effective energy transfer in such quantum dots, in particular, ZnSe/ZnS QDs donor–acceptor systems. Thus, we have initiated research on heavy metal free core-shell ZnSe/ZnS QDs as energy donors and a novel organic dye as acceptor by FRET phenomenon.

Owing to great potential and vast applications of highly conjugated oxadiazoles containing donor- π -acceptor chromophores, good deal of work has been dedicated to the study of sensitizers in OLEDs, dye-sensitized solar cells and hardly as fluorescence sensors [40]. Most of these reports confine their focus on optoelectronic applications. However, to the best of our knowledge, the applicability of 1,3,4-oxadiazole chromophore itself as an acceptor counterpart in the FRET course with core-shell ZnSe/ZnS QDs has not been reported earlier. The present work deals with design and synthesis of novel 2TVPO chromophore along with detailed study of spectroscopic, optoelectronic and thermal properties. Apart from this, the spectroscopic signature of this optoelectronically important bipolar molecule (2TVPO) during excitation via FRET from ZnSe/ZnS QDs is also explored.

2. Experimental Section

2.1. Materials: All chemicals/starting materials of reagent/analytical grade are purchased from Sigma-Aldrich and used without further purification. All solvents were freshly distilled over appropriate drying reagents prior to use during the synthesis. Heavy metal free ZnSe/ZnS-405 and 425 (7 and 8 nm) core-shell QDs dispersed in toluene were purchased from Mesolight LLC., USA. All the organic solvents used were of spectroscopic grade

(HPLC grade, Fluka), transparent, nonfluorescent in the range of excitation and fluorescence emission and used as received.

2.2. Instrumentation and experimental methods

Physical Measurements: FT-IR spectra were measured as KBr pellets on a ThermoFisher Nicolet 6700 FT-IR spectrometer in the region of 4000-400 cm⁻¹ at 2 cm⁻¹ resolution with 100 scans. ¹H and ¹³C NMR were recorded on Bruker 400-MHz FT NMR spectrometer in CDCl₃ by using TMS as internal standard. Chemical shifts are reported in ppm downfield (δ) from TMS. Melting points were determined by open capillary method and are uncorrected. High resolution mass spectra (HRMS) were obtained on Agilent Technologies 6538 UHD Accurate-Mass Q-TOF LC/MS spectrometer. Cyclic voltammetry experiments were conducted in a standard one-compartment cell in acetonitrile solvent (Spectrochem, HPLC grade). Thin films on ITO used as working electrode, platinum as counter electrode and Ag/AgCl as reference electrode respectively at a scan rate of 50 mV s⁻¹. DSC and TGA were performed with a TA Instruments DSC Q20 V24.10 Build 122 and TA Instruments SDT Q600 V20.9 Build 20, respectively, under nitrogen with heating rates of 10 °C min⁻¹.

Steady state measurements: The absorption spectra were measured with a commercial dualbeam JASCO UV-Vis NIR spectrophotometer (Model V-670). Photoluminescence spectra (PL) were collected with a spectrofluorometer (JY Horiba, Floromax-4) using an integration time of 1 s nm⁻¹, resolution of 1 nm, an excitation slit width of 2 nm and emission slit width of 2 nm. For PL measurements in solid phase, the 2TVPO chromophore film was prepared by using 5% 2TVPO solutions in chloroform, which was spin-coated on quartz slides at about 1000 rpm, for 40 s, at room temperature.

Time resolved measurements: The fluorescence lifetimes were measured employing picosecond time domain spectrometer based on Time Correlated Single Photon Counting (TCSPC) technique (IBH Jobin Yvon 6.1). The decays were collected over 1024 channels with at least 10,000 photons in the peak maximum for the lifetime experiments. The samples of core-shell ZnSe/ZnS quantum dots were excited at 280 nm and 2TVPO dye in all solvents at 415 nm, using pulsed excitation source (NanoLED) in an IBH Fluorocube apparatus. The fluorescence emission at the magic angle of 54.7° was dispersed in a monochromator (f/3) aperture to eliminate the contribution from anisotropy decay and counted by a Hamamatsu Micro Channel Plate Photo-multiplier tube (R3809 MCP-PMT). The instrument response function (IRF) for this system is ~844 ps. The fluorescence decay curves were deconvoluted

and analyzed on IBH (DAS-6) decay analysis software. From the deconvoluted fluorescence lifetime data the average fluorescence lifetime $\langle \tau \rangle$ was calculated from the following equation [35]:

$$<\tau>=\frac{\sum A_{i}\tau_{i}}{\sum A_{i}} \tag{1}$$

in which A_i is the relative amplitude corresponding to the ith decay component having the characteristic decay time constant τ_i . The acceptability of the fits was judged from the χ^2 criterion and the residual of the fitted functions to the actual data.

2.3. Quantum yield calculation

Fluorescence quantum yield (Φ) was measured at room temperature using Coumarin 480 (2,3,5,6-1H,4H-Tetrahydro-8-methylquinolizino-[9,9a,1-gh]-coumarin) as standard reference (λ_{abs} =389, λ_{em} =457 nm, Φ_R =0.95 in ethanol [41]). For all the samples, Φ , was calculated in the manner detailed by Lakowicz and Rhys Williams et al. [35,42], accounting for the refractive index of the solvent, the integrated fluorescence intensity and the absorbance at the excitation wavelength, with respect to the reference in the following equation.

$$\Phi = \Phi_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2}$$
(2)

where I is the integrated fluorescence intensity, OD is the optical density and n is the refractive index of the solution, the subscript R refers to the standard reference fluorophore of known quantum yield.

2.4. Synthesis and Characterization of novel fluorescent derivative

The required intermediates, 2-(4-tert-butylphenyl)-5-p-tolyl-1,3,4-oxadiazole (**OXD**), 2-(4-(bromomethyl)phenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (**1**) and Wittig salt (**2**) were synthesised according to our previous work [10 and references therein]. The detailed procedure is given in the ESI[†].

Synthesis of (4-((E)-2-(5-((E)-4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)styryl)thioph en-2-yl)vinyl)phenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (2TVPO):

A mixture of Phosphonium salt (2) (1g, 0.00158 mmol) and thiophene-2,5dicarbaldehyde (0.42 g, 0.00315 mmol) were taken in Water:DCM (40:60) mixture under vigorous stirring. Sodium hydroxide solution (50%, 0.65 ml) was added to the mixture by syringe and stirred for 5-6 h at room temperature. Completion of reaction was confirmed by

TLC. The reaction mixture was diluted with dichloromethane and water. The organic layer was separated and the solvent was removed under reduced pressure. The resulting solid was dried and recrystallized from ethanol to get the desired product in 70-80% yield. The synthetic approach is highly convenient and provides compound 2TVPO in the *trans* configuration across the double bond. The *trans* configuration is evidenced by ¹H-NMR spectroscopy. The compound 2TVPO displayed a doublet signal around 6.5-7.5 ppm with a typical coupling of ca. 16.00-16.60 Hz. This value corresponds with the expected value for a ³*J*trans Coupling of the vinylic protons. Further evidence concerning the structure of 2TVPO was obtained by ¹³C-NMR. The good accordance between calculated and expected values for microanalysis gives a proof of the purity of the material.

Yellow solid; Yield: 80 %; m.p. 210-215 °C; FT-IR (KBr, cm⁻¹): 3082 (-C=C-H), 3028 (C-H aromatic), 2957, 2928 (C-H aliphatic), 1605, 1547, 1490, 1415 (C=C and C=N Aromatic), 1016, 962 (1,3,4-oxadiazole ring), 933 (Thiophene ring), 842 (tert-Butylbenzene); ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.4 Hz, 4H, Ar-CH), 8.08 (d, *J* = 8.6 Hz, 4H, Ar-CH), 7.63 (d, *J* = 8.4 Hz, 4H, Ar-CH), 7.56 (d, *J* = 8.5 Hz, 4H, Ar-CH), 7.33 (d, *J*_{trans} = 16.0 Hz, 2H, *trans*-CH), 7.06 (s, 2H, Thiophene-CH), 6.97 (d, *J*_{trans} = 15.8 Hz, 2H, *trans*-CH), 1.38 (s, 18H, Ar-C(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 164.65, 164.26, 155.27, 140.12, 129.62, 128.28, 127.62, 127.33, 127.23, 126.83, 126.10, 124.64, 123.84, 121.15, 31.15, 29.72; HRMS: *m*/*z* [M + H]⁺ calc'd for C₄₄H₄₀N₄O₂S 688.8790, found 688.8935.

3. Results and discussion

Firstly, it is important to overview the spectroscopic/photophysical behavior of the novel compound (2TVPO), which is being used as an acceptor counterpart in the FRET study, with a view to understand its optoelectronic importance.

3.1. Synthesis and characterization

A quite efficient and simple synthetic procedure was used for the synthesis of compound 2TVPO as shown in **scheme 1**. The required starting material 2-(4-tert-butylphenyl)-5-p-tolyl-1,3,4-oxadiazole (**OXD**) was synthesized by the treatment of 4-methylbenzohydrazide with 4-tert-butylbenzoic acid in refluxing POCl₃. The allylic bromination of OXD with N-Bromosuccinimide in the presence of dibenzoyl peroxide at refluxing carbon tetrachloride (CCl₄) results in the formation of target compound 2-(4-(bromomethyl)phenyl)-5-(4-tert-

butylphenyl)-1,3,4-oxadiazole (1). The nucleophilic substitution reaction of triphenylphosphine at the functionalized allylic carbon leads to the formation of phosphonium ion (2) at 80 °C in DMF. Deprotonation of (2) by aq. NaOH gives ylide (Wittig reagent) in DCM and water. The vlide, acting as a nucleophile, adds to carbonyl carbon of thiophene-2,5-dicarbaldehyde. The resulting alkoxide oxygen added to the phosphorus in an intramolecular closure reaction to form four-membered ring (oxaphosphetane). The ring fragmentation leads to the formation of triphenylphosphine oxide and the desired product **2TVPO**. The resulting molecule was then purified using column chromatography on silica gel followed by recrystallization in ethanol. The nature of 2TVPO is amorphous and can be preserved for longer time under ambient conditions without any detectable decomposition. The structural identities and purities were characterized by ¹H NMR, ¹³C NMR, FT-IR, HRMS (ESI[†]) which were found to corroborate well with the proposed structure.



Scheme 1. Synthetic route for the target compound 2TVPO

3.2. Spectroscopic properties of 2TVPO

Absorption and fluorescence spectra: The photophysical properties of novel compound

2TVPO are studied in several organic solvents using UV-Vis absorption, photoluminescence (PL) and time resolved spectroscopy. The complete details are given in Fig. 1 and 2 and **Table 1.** 2TVPO exhibited solvent polarity independent, broad and structureless absorption band with two distinct peaks in all the solvents. The broad absorption bands observed at longer wavelength around 370-450 nm were assigned to the $\pi \rightarrow \pi^*$ electronic transition of whole bipolar molecule and those observed around shorter wavelength were attributed to $\pi \rightarrow$ π^* transition of 2,5-di(4-*tert*-butylphenyl)-1,3,4-oxadiazole units of the compound [43]. Broad absorption bands indicate that multiple optical transitions are contributing to the intense band in the region 375-455 nm [44]. The electronic structure of the newly synthesized molecule can be studied by PL spectra. The compound 2TVPO has exhibited spectral profiles that are independent of excitation (i.e. ~240, 300 or 425 nm), with λ_{em} around 485 nm indicating that fluorescence occurs only from the S₁ state in 2TVPO probe. The maximum fluorescence intensity was noticed under the excitation at around 425 nm. In addition, significant Stokes shift is observed for the compound 2TVPO which might be attributed to its intramolecular rotation upon photo-excitation. It has been demonstrated that incorporating a rotational substituent in a fluorophore molecule with tailored steric hindrance effects and resonance effects leads to a substantial increase in the Stokes shift in many dye molecules [45].

A typical PL spectrum of 2TVPO in both solution (toluene) and solid phase is shown in **Fig. 3**. Solution phase emission spectrum is broader and structureless, having *FWHM* of 65 nm. The compound is highly green emissive solid with emission maxima at 552 nm. A red shift of around 77 nm in the solid phase is observed when compared with toluene solution of the 2TVPO compound. Thus the compound emits intense green color in solution and yellow color in solid phase. The red shift could probably be related to aggregation effects and certain solid state molecular morphology imposed by the donor and acceptor units of 2TVPO.

Salvatochromism of 2TVPO: Solvatochromic behavior of 2TVPO has been studied in polar protic solvents (methanol-decanol), nonpolar solvents (chloroform, toluene, dichloromethane (DCM)) and polar aprotic solvents (dimethylsulfoxide (DMSO), dimethyleformamide (DMF)) in order to understand the intramolecular charge transfer (ICT) effect as summarized in **Table 1** and **Figs. 1** and **2**. The shift in λ_{abs} and λ_{em} values with respect to solvent polarity reflects the molecular interactions between solute and solvent. The molar absorptivities, ε , of aqueous 2TVPO were determined at around 425 nm. An absorption having high molar absorptivities ($\varepsilon = 2.60-3.57 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) at lower energies, occurs for 2TVPO with

strong allowed $\pi \rightarrow \pi^*$ transitions. However, the spectra show moderate band shift (~10 nm) up on changing solvents from methanol to toluene (blue shift) as illustrated in Fig. 1 and **Table 1**, though the molar absorptivities differ slightly. It should be noted that the observed differences in molar absorptivity of 2TVPO is mainly due to its solubility in aqueous solutions. The small shift in absorption band as a function of solvent polarity is due to the small change in polarity of the ground state of solvated 2TVPO (see Table 1). It indicates that the ground state energy distribution is not affected to greater extent as 2TVPO is less polar in that state. However, solvent polarity has a slight effect on the peak positions of the electronic emission maxima (~24 nm). Increasing solvent polarity leads to a red shift in the PL maxima owing perhaps to the reasonable difference between charge distributions in the ground and excited states of solute which results in a strong interaction between polar solvents and 2TVPO in the excited state. This sensitivity of dye to the selected organic solvents is due to ICT between the thiophene (electron donor) unit and the oxadiazole (electron acceptors) units in the excited state. This results a slight increase in excited state dipole moment (i.e., $\mu_e > \mu_g$). This dipole interacts with the dipole of polar solvent molecules to reduce the excited state energy and hence results in bathochromic shift. During ICT, bathochromic shift also occurs due to net stabilization of the excited state as compared to the ground state with increasing solvent polarity [46]. Generally, a small Stokes shift leads to larger overlap between the absorption and emission spectra causing self absorption of the emitted light and decreased fluorescence efficiency. Interestingly, 2TVPO chromophore exhibited large Stokes shift values (~52-66 nm), indicating substantially reduced selfabsorption. Stokes shift value is found to increase with polarity of solvent, implying a charge transfer transition and an increased dipole moment in the excited state (i.e., $\mu_e > \mu_g$). This indicates that the PL emission is from a more polar ICT state.

Generally, for ICT chromophores, the solvent polarity has significant effect on the fluorescence quantum efficiency (ability to emit light) because ICT in itself is a quenching factor which promotes the nonradiative decay rate. Particularly, in more polar solvents, ICT stabilizes charge separation and results in low quantum yields (QY). This kind of effect is observed for 2TVPO fluorophore, the QY of which is around 47–62% in solvents such as DMSO, DMF, chloroform, DCM and toluene. Further, the fluorescence QY decreased drastically in polar protic solvents like methanol and ethanol (**Table 1**). This is possibly due to the interaction between the protic solvents and the excited state and fluorescence quenching. It may be noted that the fluorescence quenching of many molecules having ICT

states results from the deactivation via internal conversion ensuing from hydrogen bonding [44, 47-49].

The abrupt change in the dipole moment is one of the principal reasons for spectral shifts in steady state solvatochromism, whereas the conformational stability of excited state is determined by fluorescence lifetimes [50-51]. Usually, the lifetimes increase with solvent polarity for stabilized excited state. Fluorescence lifetimes were measured in solvents of different polarity varying from polar to nonpolar (methanol to toluene) (**Fig. 2**). The fluorescence lifetime of 2TVPO appears to decrease as the solvent polarity increases in selected solvents from decanol to methanol (see **Table 1**). However, in DMSO, DMF, chloroform and DCM, it is shorter than those in alcohols (butanol-decanol) and showing slight nonlinear trend with solvent polarizibility, indicating that the stability of the excited state also could be affected by solvent viscosity [52]. The shorter lifetimes in methanol and ethanol are due to a strong interaction between protic solvents and 2TVPO probe (hydrogen bonding between the ICT state of 2TVPO and solvents) [47-48].

3.3. Thermal properties

The formation of morphologically stable material films is a key requirement for the operation of organic electronic devices. For the creation of stable organic devices, it is necessary to synthesize materials exhibiting high glass transition temperatures (T_g) which ensures that no phase transition will occur upon operation. It is obvious that the morphological and thermal stability are closely correlated to the molecular size and weights. The corporation of the tertbutylphenyl unit significantly improves the T_{5d} and T_g as compared to previously reported bipolar molecules without such substitution [9]. The morphological and thermal stabilities of compound 2TVPO were characterized by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are depicted in Fig. S18 and Table S1 (ESI). DSC was carried out from 25 to 400 $^{\circ}C$ under N_2 with heating rate of 10 $^{\circ}C/min.$ The phase transition properties of 2TVPO were analyzed using DSC which reveals that the molecule is crystalline in nature. The DSC curve exhibits an endothermic baseline shift related to the glass transition temperature (T_g) at 254.4 °C. It is interesting to note that, the T_g of 2TVPO is significantly higher than those of well-known oxadiazole based electron transporting materials, like 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole ($T_g=60^{\circ}C$), 1,3bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl] phenylene ($T_g=77^{\circ}C$) and also than the nonbipolar host emitters that include oxadiazoles (BOBP, $T_g=45^{\circ}C$; TPOs and PPOs, T_{gs} up to $121^{\circ}C$) [9]. The 2TVPO is a material, crystalline nature and having sharp endothermic melting peaks

at 313.6 and 322.3 °C in the thermogram. The peaks corresponds to exothermic were absent at higher temperature which indicates that 2TVPO has crystallization nature with excellent amorphous glass state stability. TGA result revealed that the 2TVPO is thermally quite stable with 5% weight loss temperatures (T_{5d}) at 378 °C and hence 2TVPO is exhibiting good thermal stability. Thus, the compound is potential material for making stable devices in photovoltaic and optoelectronic applications.

3.4. FRET from core-shell ZnSe/ZnS QDs to novel fluorescent derivative 2TVPO

3.4.1. Steady-state measurements

The ZnSe/ZnS nanocrystals exhibit unique photophysical properties like broad absorption spectra, narrow and symmetric emission spectra and high PL quantum yields [39,53]. These were selected as donors with 2TVPO as acceptor in order to enhance the overlap of the donor emission and acceptor absorption spectra as it is a prerequisite to get any measurable FRET (eqn. (S3)). The size of QDs offers a unique advantage to control this parameter, which in turn can regulate the efficiency of FRET. Further, this overlap can also be controlled by altering the composition of QD and thereby varying its emission when paired with an acceptor dye [53-55]. This distinct aspect is illustrated in Fig. 4 where the PL emissions of two different sizes (7 and 8 nm) of heavy metal free ZnSe/ZnS-405 and 425 core-shell quantum dots (QD1 and QD2) emitting violet color at 406 and 418 nm are plotted along with the absorption spectrum of 2TVPO dye. The 2TVPO probe has absorption peak at 425 nm, thus making the present pair perfectly suited for FRET process. The photophysical properties of two FRET pairs selected based on the changing size of core/shell QD donors are listed in Table 2. The excitation wavelength was fixed at 330 nm for all samples to avoid direct excitation of the acceptor (see Fig. 4), as the absorption of 2TVPO is negligible at 330 nm and therefore a clear photoinduced resonance energy transfer is possible from donor to acceptor. Inset of Fig. 4 shows the extent of overlap functions, $J(\lambda)$ which describes the effects of size of the QDs and its emission on the degree of spectral overlap for a given acceptor chromophore. Evidently, absorption spectra of 2TVPO overlaps well with the QD2 donor fluorescence spectra as compared to QD1 (Table 3). With increasing overlap integral an expected proportional increase in the value of R_0 is seen (eqn. (S5) which together with the high QY of the QDs helps in efficient FRET at longer distances of separation.

Fig. 5 depicts gradual decrease in the PL intensity of donor ZnSe/ZnS QDs and a simultaneous enhancement of the emission intensity of acceptor 2TVPO with increasing the concentration of 2TVPO (1 to 9 μ M). The reduction in QDs emission intensity and increase

in 2TVPO dye emission (at around 500 nm) confirms the nonradiative energy transfer from QDs to 2TVPO dye. The new emission peak at around 500 nm corresponds to the 2TVPO dye arising via FRET from QDs to dye. The fluorescence intensity of 2TVPO fluorophore increases due to an increase in the FRET efficiency from QD to dye. Interstingly, the emission intensity of the 2TVPO dye bound to the QDs is more than nearly six times larger than when excited directly, indicating sensitized acceptor fluorescence due to FRET. All these observations demonstrate that the steady state emission of 2TVPO in the presence of QD1 and QD2 originates through FRET. Additionally, this Förster type resonance energy transfer from QDs donor to 2TVPO acceptor bears excellent consistency with earlier reports of Martynenko et al. [1], Hering et al. [34], Lakowicz [35], Shu et al. [39] and our own works [53-55].

Further, it is of interest to note that the concentration of the acceptor (2TVPO) required is rather too low ($\sim\mu$ M) in the medium for FRET to occur with estimable efficiency (**Fig. 5**). However, this can be explained as due to high quantum yield of 2TVPO in toluene medium (**Table 1**). Now, remembering the essential role of FRET on the immensely significant aspects of photo-sensitization [1-2], energy-conversion processes [3] etc., it is logical to focus the present investigation on the highly fluorescent 2TVPO chromophore to elucidate the key role of FRET in its emission at longer wavelength via FRET. Hence, the use of fluorescent 2TVPO probe in FRET based applications and photosensitization in aqueous medium could be interesting.

It is well known that FRET efficiency (ET) varies as function of overlap integral of QDs and dye fluorophore [35, 54-56] and the molecular proximity of donor–acceptor in the mixture [57]. It has been observed that the ET varies almost linearly with increase in acceptor (2TVPO) concentration. This linear variation is due to the possible contribution of Förster type energy transfer and close proximity of the QDs and 2TVPO. The FRET parameters viz., spectral overlap integral $J(\lambda)$ (eqn. (S3), Förster radius R_0 (eqn. (S5), the donor-acceptor distance r, ET (eqn. (S8) and transfer rate $k_T(r)$ (eqn. (S1) have been calculated from the spectral characteristics of donor-acceptor mixture and listed in **Table 3.** We observed that ET is 34.83% for core–shell QD1-2TVPO pair and it is less compared to 55.02% noted in case of QD2-2TVPO pair. This difference can be well explained by FRET parameters. The values of R_0 obtained for present FRET pairs QD1-2TVPO and QD2-2TVPO are 6.20 and 6.59 nm respectively, which strongly depend on the QY of the donor and overlap. It is noticed that R_0 linearly increases with the increase in the overlap and that r decreases with the increasing $J(\lambda)$

distances, it is evident that these FRET couples are well suited for investigation of conformational changes in the molecules and/or detecting the interactions between the molecules [35]. Therefore, all the FRET parameters obtained for donor-acceptor pair as well as size of donor QDs play a significant role in influencing the ET.

3.4.2. Time resolved fluorescence study

The steady state fluorescence measurements of the donor-acceptor pairs give an average and relative representation about FRET. A better confirmation is, however, could be derived from time resolved measurements which give an absolute measure (independent of concentration and fluctuations in excitation source intensity) and provide a clear dynamic picture of the fluorescence. In order to obtain quantitative confirmation for the FRET from QDs to 2TVPO, the PL decays of the donor (QD1 and QD2) were examined in the absence and presence of 2TVPO. Fig. 6 shows PL decays dynamics of QDs alone and QDs-2TVPO mixture when excited with λ_{exc} = 280 nm at 300 K. The fluorescence decays contain two components (fast and slow) (see Table 4). Therefore, decay profiles are best stated by bi-exponential function, $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 represent the fast and slow decay times, respectively and A₁ and A₂ are the corresponding contributions to the total fluorescence intensity and accordingly their average lifetime is calculated using by eqn.(S9). This origin of bi/tri/multiexponential PL decay profile of semiconductor quantum dots is still not clear. The faster decay is due to radiative relaxation of the excited electron and is attributed to initially populated core-shell recombination [54-56, 58-59]. However, the possible origin of long and longer radiative decays remains relatively uncertain. Thus multiexponential nature of the PL decays and the average lifetimes of the QDs are consistent with the literature.

As listed in **Table 4**, the PL decay profiles of the donor (QDs) in the absence and presence of the acceptor (2TVPO) are analyzed by a bi-exponential function with the average lifetimes of donor QD1 and QD2 without the 2TVPO dye being 6.78 and 6.92 ns, respectively. The acceptor induced changes in lifetimes of QD1 and QD2 are found to conform by decreasing lifetimes in presence of 2TVPO (9 μ M), reaching to 5.28 and 4.14 ns in QD1 and QD2, respectively (**Table 4**). Shortening of decay time is perceived with decrease in both components (τ_1 and τ_2) which confirms that nonradiative energy is transferred via FRET to 2TVPO dye. Thus FRET offers an alternative pathway for donor relaxation, reducing its lifetime in the presence of acceptor 2TVPO. For QDs with high fluorescence QY, the amplitude (A₂) with the longest lifetime component dominates the total PL. In other words, holes and electrons have greater probability of being on the QDs surfaces

contributing to the longest lifetime. Thus, it implies that the surface of QDs is certainly involved in the process of energy transfer via FRET [54-56]. The transfer efficiency values determined using the time resolved data from eqn. (S8) are 22.08 and 40.25% for QD1 and QD2 to 2TVPO dye, respectively. Further, it has been observed that these values are smaller than ones obtained from steady state studies. This is due to the fact that time resolved data are independent of fluctuations in the excitation source intensity and concentration (see Table 4).

3.4.3. Fluorescence quenching of QDs in the presence of 2TVPO

The Stern–Volmer (SV) plots were analyzed for both steady state and time resolved measurements to get better insight into the type of quenching in the FRET. The SV equation (eqn. (3) relates concentration of quencher and excited states quenching [56, 60] as follows:

$$\frac{F_D}{F_{DA}} = 1 + K_D[Q] = 1 + k_q \tau_D[Q] = \frac{\tau_D}{\tau_{DA}}$$
(3)

where F_D and F_{DA} are the PL intensity of donor (QDs) in the absence and presence of quencher (2TVPO), K_D is the SV quenching constant, k_q is the rate constant of the bimolecular process, [Q], the quencher concentration while τ_D and τ_{DA} are the average lifetimes of the donor with and without the quencher, respectively. In many cases, the chromophore may be quenched either by static or by dynamic quenching. In case of static quenching, complex formation occurs between the chromophore and quenchers in the ground state. This certainly affects PL intensity but not on the lifetimes. However, dynamic quenching signifies collision between the chromophore and quenchers during the excitation of the chromophore. Consequently, the PL lifetime is shortened.

When 2TVPO dye (from 1 to 9 μ M) was gradually added to the ZnSe/ZnS QDs solution of fixed concentration, a decrease in the PL intensity of QDs was noticed. This quenching is described in the SV plots for both steady state and time resolved studies (**Fig. 7** (**A**, **B**, **C** and **D**)). Note that F_D/F_{DA} and τ_D/τ_{DA} versus [Q] vary linearly with increasing concentration of quencher, suggesting that dynamic quenching is involved in the ZnSe/ZnS QDs-2TVPO systems. The SV quenching constant (K_D) obtained from the slopes of these graphs are $6.02 \times 10^4 M^{-1}$, $11.15 \times 10^4 M^{-1}$ and $3.20 \times 10^4 M^{-1}$, $7.31 \times 10^4 M^{-1}$ for QD1 and QD2 to 2TVPO in steadystate and time resolved measurements, respectively. The estimated quenching rate constant (k_q) reflects on the efficiency of quenching or the accessibility of the probes to the quencher. The k_q values thus determined are 8.9×10^{12} , $16.1 \times 10^{12} M^{-1}S^{-1}$ and 4.7×10^{12} , $10.5 \times 10^{12} M^{-1}S^{-1}$ for these FRET pairs in steady state and time resolved

measurements, respectively. Further, the diffusion controlled quenching usually results in values of $k_q \sim 10^{10} M^{-1}S^{-1}$ as expected from the Smoluchowski eqn. $(k_{diff} = 8RT/3\eta)$ [61]. Values of k_q smaller than the diffusion limited rate constant can result from steric shielding of the fluorophore or a low quenching efficiency. However, in the present study the values of k_q estimated from the SV equation are quite larger than the diffusion limited rate constant. Hence, it is inferred that this is not a diffusion controlled process [35].

4. Concluding remarks

A novel fluorescent highly conjugated 1,3,4-oxadiazole containing donor- π -acceptor chromophore molecular system viz., 2TVPO has been synthesized through a relatively simple synthetic protocol (Wittig reaction) and its spectroscopic and electrochemical aspects are investigated in detail. The structure of this newly synthesized compound was confirmed by their analytical and spectral data. The thermal and morphological stabilities of this compound were found to be good at higher temperatures. The compound 2TVPO is then employed as acceptor moiety in the study of FRET from core-shell ZnSe/ZnS QD as donors. A combined application of steady-state and time-resolved fluorescence spectroscopic tools has been used to confirm the occurrence of FRET process via long-range dipole-dipole interaction. This study clearly illustrates that the energy transfer efficiency linearly varies with spectral overlap, size of QDs and quantum yield of the donor. It is found that transfer efficiency is higher for ZnSe/ZnS-425 QD (8 nm) compared to that of ZnSe/ZnS-405 QD (7nm). Additionally, the values of SV and bimolecular quenching constants determined experimentally inferred that quenching is not a diffusion controlled process. The results demonstrate that the novel D- π -A chromophore might play an important role in organic optoelectronics and FRET based sensing applications. Further, ZnSe/ZnS QDs are free from toxic heavy metals like cadmium, selenium, etc., which allows the exploration of their possible applications as safer donors for FRET in various biological applications.

Supporting Information Summary

Supporting information includes the following details;

(a) Experimental section describing the synthesis of intermediates, (b) Analytical and spectroscopic data viz.,1H NMR, 13C NMR, HR-MS, FT-IR, for all intermediates and titled compound (c) optical band gap study, (d) electrochemical properties, CV measurements, (e) DSC and TGA thermograms and (f) theory of FRET measurements.

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Figure 1.Normalized absorption and emission spectra of 2TVPO in (**A**) alcohols (methanoldecanol) and (**B**) general solvents at room temperature.

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Figure 2. Typical time resolved fluorescence decays profiles of 2TVPO in (**A**) alcohols (methanol-decanol) and (**B**) general solvents. The sharp gray profile on the extreme left represents the instrument response function (IRF). 1 Channel=0.02743484 ns.



Figure 3. Typical normalized PL spectra of 2TVPO in (1) toluene solution (solid black line) and (2) Solid phase (dashed red line), excited at 425 nm.

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Figure 4. Overlap between absorption spectra of 2TVPO (dotted line) and PL spectra of [**a**] ZnSe/ZnS-405 QD (solid black line) and [**b**] ZnSe/ZnS-425 QD (solid red line) in toluene at room temperature. The inset shows plots of the resulting overlap functions $J(\lambda)$. The size of QDs can substantially improve the degree of spectral overlap with the 2TVPO.



Figure 5. Representative steady-state PL profile of [A] ZnSe/ZnS-405 QD and [B] ZnSe/ZnS-425 with incremental addition of 2TVPO (λ_{exc} =330 nm). Curves (a-h) correspond to 2TVPO [(a) QD alone, (b) 1 μ M, (c) 2 μ M, (d) 3 μ M, (e) 5 μ M, (f) 7 μ M, (g) 8 μ M, (h) 9 μ M]. The enhanced emission above 450 nm corresponds to the 2TVPO resulting from energy transfer from the QDs



Figure 6. Log scale plot of time-resolved PL traces for **[A]** ZnSe/ZnS-405 QD and **[B]** ZnSe/ZnS-425 QD with and without 2TVPO dye.

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Figure 7. (A) & (B) are steady state Stern-Volmer plot of $F_0 \setminus F$ vs. concentration of quencher, (C) & (D) are time resolved Stern-Volmer plot of τ_0/τ vs. concentration of quencher for FRET pairs ZnSe/ZnS-405 (QD1)-2TVPO and ZnSe/ZnS-425 (QD2)-2TVPO.

Solvent	$\lambda_{abs}^{[a]}$ (nm)	$\mathcal{E}_{abs}^{[b]}$ (×10 ¹ M ⁻¹ cm ⁻¹)	$\lambda_{\rm em}^{[a]}$ (<i>nm</i>)	Δλ (nm)	Φ _f (%)	τ _f (ns)
Methanol	435	26100	501	66	22	0.536
Ethanol	433	26000	496	63	31	0.640
Butanol	431	27300	494	63	34	0.725
Pentanol	430	27100	491	61	32	0.759
Hexanol	430	28900	490	60	36	0.787
Heptanol	429	29000	488	59	41	0.811
Octanol	428	29500	487	59	41	0.836
Nonanol	427	29500	486	59	40	0.849
Decanol	427	29600	486	59	43	0.858
DMSO	432	29900	490	58	48	0.672
DMF	430	28500	488	58	47	0.649
Chloroform	429	32000	482	53	53	0.717
DCM	428	31100	481	53	51	0.688
Toluene	425	35700	477	52	62	0.878

Table 1. Spectroscopic properties of 2TVPO in various solvents at 300 K.

[a] The spectra were measured in selected organic solvents at $1\mu M$ concentration. [b]The molar absorption coefficient was measured in solution.

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Table 2.

Photophysical properties of ZnSe/ZnS QDs.

QD	Size (<i>nm</i>)	$\lambda_{exc}(nm)$	λ_{emi} (nm)	$arPhi_f(\%)$
ZnSe/ZnS-405	7	330	406	62
ZnSe/ZnS-425	8	330	418	70
				S

FRET Pair	$J(\lambda)$ $(M^{-1}cm^{3} \times 10^{-13})$	<i>R</i> ₀ (<i>nm</i>)	r (nm)	Efficiency (%)	Transfer rate $k_T(r) S^{-1}$
ZnSe/ZnS-405-2TVPO	7.84	6.20	6.88	34.83	7.9×10 ⁷
ZnSe/ZnS-425-2TVPO	10.03	6.59	6.37	55.02	17.7×10 ⁷
		7	4	50	
		Ng.			
	TE				
C	CEP				
PL					

Table 3. FRET parameters obtained from steady-state measurements.

FRET Pair	$ au_1$ (ns)	$ au_2$ (ns)	A ₁	A ₂	Average $<\tau>(ns)$	Efficiency ^[a] (%)	Efficiency ^[b] (%)
ZnSe/ZnS-405	2.68	7.59	16.6	83.4	6.78	RP	
ZnSe/ZnS-405-2TVPO	1.81	5.81	13.28	86.72	5.28	22.08	34.83
ZnSe/ZnS-425	2.45	7.85	17.13	82.87	6.92		
ZnSe/ZnS-425-2TVPO	1.10	4.61	13.45	86.55	4.14	40.25	55.02

Table 4. FRET parameters obtained from time-resolved measurements.

[a] obtained from time-resolved measurements. [b] obtained from steady-state measurements.

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Graphical abstract



Highlights

- A novel, high quantum efficiency green fluorescent 1,3,4-oxadiazol molecule was synthesized.
- Photophysical, thermal and electrochemical properties of this novel probe were studied in depth.
- New FRET pair comprising core-shell ZnSe/ZnS quantum dots as donor and 2TVPO as acceptor developed.
- The system exhibits a Förster distance of ~6 nm and high FRET efficiency of ~55%.

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