

TD-DFT Investigation of 2,5-Bis-(2-benzothiazolyl)hydroquinone and 2,5-Bis(benzo[d]thiazol-2-yl)-4-methoxyphenol

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Received: 10 July 2016/Accepted: 1 January 2017 © Springer Science+Business Media New York 2017

Abstract Density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculations of two excited state intramolecular proton transfer (ESIPT) molecules [2,5-bis(2-benzothiazolyl)hydroquinone and 2,5-bis(benzo[d]thiazol-2-yl)-4-methoxyphenol] were performed to study their structural and photo-physical behavior upon excitation. The most stable structure was established by optimizing all possible rotamers. The vertical excitation and emission wavelengths obtained by using TD-DFT show very good correlation with the experimental values. A correlation has been established based on the absorption values to determine the contribution of stable rotamers.

Keywords ESIPT · DFT · TD-DFT · 2,5-Bis(2-benzothiazolyl)hydroquinone · 2,5-Bis(benzo[d]thiazol-2-yl)-4-methoxyphenol

Electronic supplementary material The online version of this article (doi:10.1007/s10953-017-0628-5) contains supplementary material, which is available to authorized users.

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1 Introduction

Molecules exhibiting excited-state intermolecular proton transfer (ESIPT) phenomenon have emerged as functional materials after the pioneering work of Weller [1, 2]. The environmental dependence of the spectral properties and a large Stokes-shifted fluorescence associated with these molecules enhance their importance as smart molecules [3]. Upon electronic excitation, these molecules each exhibit a four-level photo-physical state [4]. Experimental and theoretical investigations have been extensively used to explore this four-level photo-physical state [5, 6]. ESIPT is a keto-enol tautomeric succession occurring in the excited state which arises from the transfer of an acidic proton from a hydroxyl or amino group to a basic acceptor such as a carbonyl oxygen or nitrogen atom in a heterocyclic compound [7, 8]. Upon electronic excitation, abrupt enhancement of the acidity of the hydroxyl or amino proton and basicity of acceptor lead to extremely fast migration of the proton to the acceptor [9, 10]. The fast delocalization of the positive charge over the heterocyclic ring in the excited state results in a large Stokes-shifted keto tautomer [11, 12]. On relaxation of the keto form, the energetically preferred enol form is regenerated in a non-radiative manner by reverse proton transfer [7, 13]. Subsequently, this process leads to the momentary alternation of electronic properties such as electron density distribution, energies of electronic states and dipole moments. Emission from the keto state gives rise to a large Stokes-shifted emission [14, 15] which is of importance in the fields of laser dyes [16], fluorescent probes [17, 18], photo-chromic dyes [19], sensors [20], organic electroluminescence [21, 22], pH sensor [23], optical materials and organic triplet photostabilizers [24].

2-(2'-Hydroxyphenyl)benzothiazole (HBT) [25–29] and its derivatives [30–32] are among the most investigated ESIPT molecules due to their applications in the fields of bioimaging, medicine, agrochemicals and sensors [17, 30, 33]. DFT and TD-DFT methods [34, 35] have been used for ground state geometry optimization and for understanding the excited state behavior of ESIPT-based benzoxazole molecules. However, there are few papers concerning 2,5-bis(2-benzothiazolyl)hydroquinone [36, 37] and its derivatives. Therefore, taking note of the potential application of these ESIPT molecules and in continuation of our research work on fluorescent materials, herein we report a TD-DFT study to understand the geometry of the different conformers of 2,5-bis(2-benzothiazolyl) hydroquinone and 2,5-bis(benzo[d]thiazol-2-yl)-4-methoxyphenol along with the dependence of their absorption and fluorescence maxima on the solvent.

2 Methodology

2.1 Experimental Section

2.1.1 Chemicals and Instruments

All the chemicals were procured from S. D. Fine Chemicals and used without further purification. The synthetic grade solvents were taken from S. D. Fine chemicals and used as supplied. The UV–Visible spectra were recorded on a Lab India UV–Vis with Model No 3000⁺ instrument. The emission spectra was recorded on a Varian Cary Eclipse fluorescence spectrophotometer.

2.1.2 Synthesis Strategy

The detailed routes for the synthesis of 2,5-bis(2-benzothiazolyl)hydroquinone and 2,5bis(benzo[d]thiazol-2-yl)-4-methoxyphenol are replicated in Scheme 1. 2,5-Dibromo-1,4dimethylbenzene was oxidized according to the reported protocol by using potassium permanganate in a hot pyridine:water (1:1) mixture to obtain compound 2 with 81% yield [38, 39]. Purification of compound 2 was carried by recrystallization from a dichloromethane:methanol (7:3) mixture. Compound 3 was obtained with 60% yield by treating compound 2 with sodium carbonate in the presence of a catalytic amount of pyridine + cuprous bromide complex in water [40]. Condensation of compound 3 was carried according to the reported protocol by using 2 equivalents of 2-aminothiophenol and ten equivalents PPA to obtain 2,5-bis(2-benzimidazolyl)hydroquinone [37] (compound 4) with 47% yield. Controlled mono-methylation, using the reported procedure, with methyl iodide in DMF in the presence of potassium carbonate, gave 2,5-bis(benzo[d]thiazol-2-yl)-4methoxyphenol [41] (compound 5) with 58% yield. Purification of compounds 4 and 5 were carried out by performing repetitive crystallization from DMF [37].

2.2 Computational Methods

The B3LYP functional [42] was employed to optimize the ground state of all possible keto-enol rotamers of compounds 4 and 5 in the gas phase and solvent. The B3LYP functional is a combination of Becke's three parameter exchange functional (B3) [43] with the nonlocal correlation functional of Lee, Yang, and Parr (LYP) [44]. The basis set 6-31G(d) [45] was used for all atoms in the ground and excited states. The local minimum and the vibrational frequency of each enol rotamer and its corresponding keto tautomer were computed using TD-DFT [46, 47] calculations using the B3LYP functional and the 6-31G(d) basis set and to obtain the optimized structure of the low-lying first singlet excited state (S1) of each conformer and its minimum energy geometry. The excited state geometries obtained from TD-DFT calculation were also used to obtain vertical excitation energies, which correspond to the emission values, using the same



Scheme 1 Synthesis of 2,5-bis(2-benzothiazolyl)hydroquinone (compound 4). Reactions and conditions of Scheme 1: a KMnO₄, 6 equivalents (two equivalents first addition + 0.5 equivalents each in eight more additions), pyridine, H₂O, 81%. b Na₂CO₃, pyridine, CuBr, H₂O, 60%. c 2-aminothiophenol, two equivalents, PPA 10 equivalents, 190 °C, 24 h, 47%. d MeI (1 eq), NaOH (1.05 eq), DMF, 80 °C, 58%

basis set. Frequency computations were also performed on the optimized geometry of the low-lying vibronically relaxed first excited state of conformers. The polarizable continuum model (PCM) [48, 49] was used for optimizations in solvents of different polarities. All electronic structure computations were performed by using the Gaussian 09 program [50].

3 Results and Discussion

3.1 Structural Parameters

Compound 4 has two hydroxyl groups at the 1 and 4 positions whereas compound 5 contains one hydroxyl and one methyl group at the 1 and 4 positions. These groups can interact with the two benzothiazole rings in the excited state by absorption of light, which leads to the possibility of having different conformer arrangements in the excited state via the rearrangement of a proton leading to excited state intramolecular proton transfer (ESIPT). Both compounds 4 and 5 can exist in enol or keto forms or as a mixture of enolketo tautomers. Due to the rotation around a single bond, compounds 4 and 5 can have interconvertible conformational isomers that may co-exist. To obtain the lowest energy of the stable conformer of compounds 4 and 5, all the possible keto-enol rotamers of compounds 4 and 5 were optimized in the gas phase and in the solvent phase using the B3LYP/ 6-31G(d) method. Compound 4 shows the possibility of having nine enol rotamers and their nine respective keto rotamers, whereas compound 5 can exist in sixteen enol rotameric forms and sixteen keto rotameric forms. Figure 1 shows all the nine enol-keto rotamers of compound 4 considered for optimization while all sixteen enol-keto rotamers of compound 5 are shown in Fig. 2. The relative energies in both $kJ \cdot mol^{-1}$ and $kcal \cdot mol^{-1}$ of all the optimized planar enol-keto rotamers for compounds 4 and 5 in the gas phase are presented in Tables 1 and 2, respectively. The relative energies of all enol and keto tautomers were obtained by subtracting the energy of the most stable rotamer from the actual energy of the each enol and keto rotamer obtained for the gas phase optimized geometries of each rotamer, using the B3LYP/6-31G(d) method.

The relative energies listed in Table 1 indicate that the R1 rotamer of compound 4 in its enol form, where the two hydroxyl groups at 1,4-positions are in close vicinity of the N=C bond of the benzothiazole ring, is the thermodynamically most stable rotamer in the gas phase. The same trend is observed in polar and non-polar solvents, while its keto tautomer has the lowest energy among all the keto conformers. The optimized enol-keto geometry of the stable conformer R1 in DMF is shown in Fig. 3 while the structural parameters are presented in Table 3. The rotamer R1 in its enol form shows the possibility of having two intermolecular hydrogen bonds between the two acidic protons of the hydroxyl groups present at the 1,4-positions and the basic nitrogen atoms of two benzothiazole rings.

The possibility of intermolecular hydrogen bonding and structural orientation of the R1 enol conformer facilitates the migration of a proton from a hydroxyl group to a nitrogen atom upon photo-excitation exhibiting the ESIPT phenomenon. The presence of ESIPT is confirmed from the structural parameters and the changes in Mulliken charges of the optimized geometries of the R1 conformer at the ground and excited state. Comparison of the relative energies confirms the enol R1 conformer as the preferred geometry of compound 4 in the ground state as compared to the other conformers.



Fig. 1 Rotameric and tautomeric species of 2,5-bis(2-benzothiazolyl)hydroquinone (compound 4)



Fig. 2 Rotameric and tautomeric species of 2,5-bis(benzo[d]thiazol-2-yl)-4-methoxyphenol (compound 5)





 Table 1
 Relative energies of all

 the rotamers of compound 4 in
 the

 the gas phase
 the

Rotamer	Relative energy of compound 4 in $kJ \cdot mol^{-1}$ (kcal·mol ⁻¹)				
	Enol	Keto			
R1	0.0 (0.0) ^a	53.6 (12.8)			
R2	53.7 (12.8)	84.9 (20.3)			
R3	105.5 (25.2)	84.9 (20.3)			
R4	57.9 (13.9)	107.9 (25.8)			
R5	114.3 (27.3)	107.9 (25.8)			
R6	91.5 (21.9)	142.3 (34.0)			
R7	67.8 (16.2)	126.4 (30.2)			
R8	39.4 (9.4)	142.3 (34.0)			
R9	91.5 (21.9)	84.9 (20.3)			

^a SN first number is in units of kJ·mol⁻¹; the second number (in *parentheses*) is in units of kcal·mol⁻¹

Table 2	Relative ene	rgies of all
the rotam	ers of comp	ound 5

Rotamer	Relative energy of compound 5 in $kJ \cdot mol^{-1}$ (kcal·mol ⁻¹)			
	Enol	Keto		
R1	19.7 (4.7) ^a	68.6 (16.4)		
R2	18.1 (4.3)	104.0 (24.9)		
R3	19.7 (4.7)	85.4 (20.4)		
R4	19.7 (4.7)	83.7 (20.0)		
R5	76.2 (18.2)	83.7 (20.0)		
R6	77.9 (18.6)	72.8 (17.4)		
R7	20.8 (5.0)	72.8 (17.4)		
R8	76.2 (18.2)	85.4 (20.4)		
R9	53.1 (12.7)	98.1 (23.4)		
R10	18.1 (4.3)	98.1 (23.4)		
R11	76.2 (18.2)	85.4 (20.4)		
R12	29.6 (7.1)	98.1 (23.4)		
R13	18.1 (4.3)	98.1 (23.4)		
R14	76.2 (18.2)	83.7 (20.0)		
R15	73.5 (17.6)	68.5 (16.4)		
R16	0.0 (0.0)	64.4 (15.4)		

^a The first number is in units of kJ·mol⁻¹; the second number (in *parentheses*) is in units of kcal·mol⁻¹

Table 3 summarizes the data, showing the variation in bond distance and bond angle of the rotamer R1 in DMF in the ground and excited states. The variation in bond angle and bond distance of the ground and excited states suggests the existence of the keto tautomer of R1. The existence of the keto tautomer is further confirmed from the emission spectra, where a major red-shifted emission peak is obtained due to the keto tautomer. The variation in Mulliken charges on atoms N31, H36, and O35 of the ground and excited state optimized geometries of the enol form and the keto form are given in Table S1 (supplementary material). The planarity of the molecule contributes substantially to ESIPT, facilitating the transfer of proton H36 in the excited state from O35 to N31.

In the case of compound 4 in DMF, the reduction in bond distance between N31 to H36 by 0.110 Å from enol (1.753 Å) to enol* (1.643 Å), which is further reduced by 0.609 Å for the enol* to keto* transition space between number and units, supports the existence of



Fig. 3 Optimized structures of compound 4: R1 conformer in enol-keto forms

ESIPT. There is an enhancement in the bond distance between H36 and O35 by 0.027 Å for enol to enol* and by 0.776 Å for enol* to keto*, respectively. This substantial incremental change in bond length between H36 and O35 from the enol to keto states suggests that in the excited state (enol*), proton H36 approaches near to N31 via intramolecular hydrogen bonding for the transfer of proton. The reduction in bond distance of the C4-C20 bond for enol (1.459 Å) to enol* (1.426 Å) by 0.033 Å, and O35-C5 bond for enol (1.353 Å) to enol* (1.326 Å) by 0.027 Å, which is further reduced by 0.057 Å in the case of keto* (1.269 Å), suggests the occurrence of the ESIPT phenomenon. In addition to these, the bond angle H36–O35–C5 increases by 0.3° from enol (107.7°) to enol* (108.0°). This confirms that H36 approaches nearer to N31 in enol*, which leads to the transfer of proton to N31 in the keto excited state (keto*) with N31-H36 bond distance 1.034 Å and O35-H36 hydrogen bonding distance of 1.796 Å. The keto* goes to the ground state keto conformer which exhibits a N31-H36 bond distance of 1.058 Å and O35-H36 hydrogen bond distance of 1.625 Å. As H36 approaches N31, in the excited state the hydrogen bond distance for H36-O35 decreases by 0.171 Å from 1.796 (keto*) to 1.625 Å (enol) and it converts to the keto conformer but then goes back to the enol ground state through nonradiative decay to complete the ESIPT process. These changes in bond distances and bond angles confirm the existence of a single ESIPT process which is supported by the redshifted emission Table 5.

Table 3 Structural parametersof conformer R1 of compound 4		Enol E ₀	Enol* E1	Keto K ₀	Keto* K ₁
in DMF obtained by optimization using the B3LYP/6-	Bond length (in Å))			
31G(d) method	N31–H36	1.753	1.643	1.058	1.034
	H36–O35	0.993	1.020	1.625	1.796
	O35–C5	1.353	1.326	1.282	1.269
	C5-C4	1.425	1.460	1.457	1.479
	C4-C20	1.459	1.426	1.419	1.421
	C20-N31	1.310	1.338	1.341	1.355
	Bond angle (in°)				
	N31-H36-O35	146.6	149.5	140.4	133.9
	H36-O35-C5	107.7	108.0	104.0	106.3
	O35-C5-C4	125.3	120.9	123.5	121.5
	C5-C4-C20	119.9	119.7	117.8	119.7
	C4-C20-N31	123.0	122.8	121.7	127.6
	C20-N31-H36	99.6	99.1	112.6	114.9

Comparison of the relative energies of all 16 enol–keto tautomers of compound 5 demonstrates that the R16 enol conformer is the thermodynamically most stable conformer in the ground state and its respective keto tautomer has the lowest energy among all the keto conformers. The optimized enol-keto geometry obtained for the stable conformer of R16 in DMF is shown in Fig. 4. The bond lengths, bond angles and dihedral angles for compound 5 are presented in Table 4. In the case of compound 5, rotamer R16, which is the most stable rotamer, has a hydroxyl group at the 1-position which lies in close vicinity to the N=C bond of the benzothiazole ring and this increases the possibility of intramolecular hydrogen bonding with the basic nitrogen atom (OH^{...}N=C). The methyl group at the four position moves away from the other benzothiazole ring to reduce the steric hindrance. Due to the presence of only one hydroxyl group, R16 can have only one intramolecular hydrogen bond. This intramolecular hydrogen bonding in R16 promotes the migration of the proton through enol-keto tautomerism upon photo-excitation to give ESIPT. The structural parameters and Mulliken charges of the ground and excited states for R16 confirm the existence of ESIPT.

The alteration in Mulliken charges on N32, H37, and O36 atoms of compound 5 upon photo excitation for the keto-enol tautomers of R16 are given Table S2 (supplementary material). The most stable rotamer R16 of compound 5 shows planarity in the region where the acidic hydrogen atom is in close proximity to the basic nitrogen, which facilitates hydrogen transfer from O36–H37 to N32 of the benzothiazole ring upon photo excitation. The proton H37 is close to N32 in the enol ground state which promotes the migration of the proton from O36 to N32. The changes in the bond distances in the optimized keto-enol tautomeric structures in the ground and excited states proves the successful transfer of acidic proton H37 to N32 to form the keto tautomer upon photo excitation. The reduction in the N32–H37 bond distance by 0.029 Å from enol (1.750 Å) to enol* (1.671 Å), compared with the increase in the bond distance between H37–O36 by 0.019 Å from enol to enol*, suggests the approach of H37 to N32 via hydrogen bonding for the transfer of the proton during photo excitation. The reduction in the C1–C9 and O36–C2 bond distances from enol to enol*, and further decrease from enol* to keto*, confirm the possibility of ESIPT. In addition to this, the increase of the H37–O36–C2 bond angle by 0.4° from enol



Compound 5: R16 Keto

Fig. 4 Optimized structure of compound 5: R16 conformer in the enol-keto forms

 (107.7°) to enol* (108.1°) suggests that the proton H37 approaches nearer to N32 in enol* and further transfers to N32 to give keto* with N32–H37 bond distance 1.035 Å and O36–H37 hydrogen bonding distance of 1.788 Å. The keto* returns to ground state keto conformer with N32–H37 bond distance of 1.051 Å and O36–H37 hydrogen bonding distance of 1.660 Å. The potential energy surfaces for compound 4 and compound 5 were obtained by changing the torsional angle (N32–C9–C1–C2) by 10°. The potential energy scans for compounds 4 and 5 are given in supporting information Figs. S9 and S10. From the potential energy scan it is evident that rotamer R1 of compound 4 and R16 of compound 5 are thermodynamically the most stable rotamers.

3.2 Photophysical Properties

Tables 5 and 6 report the correlation between the observed absorption and emission data of compounds 4 and 5 with vertical excitation and emission results obtained from the TD-DFT calculations. Compound 4 shows solvent polarity dependant absorption and emission maxima, with negative solvatochromism and negative solvatofluorism in going from non-

Table 4 Structural parameters of conformer R16 of compound 5		Enol E ₀	Enol E ₁	Keto K ₀	Keto K ₁
obtained by optimization using B3L XP/6-31G(d) method in	Bond length (in Å)				
DMF	N32-H37	1.750	1.671	1.051	1.035
	H37–O36	0.993	1.012	1.660	1.788
	O36-C2	1.351	1.333	1.278	1.270
	C2C1	1.420	1.463	1.454	1.478
	C1-C9	1.457	1.420	1.416	1.420
	C9-N32	1.310	1.341	1.357	1.357
	Bond angle (in°)				
	N32-H37-O36	146.6	149.2	134.4	134.4
	H37-O36-C2	107.7	108.1	106.1	106.1
	O36-C2-C1	123.3	120.8	121.5	121.5
	C2C1C9	120.0	120.1	119.9	119.9
	C1-C9-N32	122.9	123.1	123.3	123.3
	C9-N32-H36	99.5	98.6	114.7	114.7

polar to polar solvents; whereas, compound 5 shows negative solvatochromism and positive solvatofluorism in going from non-polar to polar solvents. Compound 4 shows five absorption maxima at 426, 392, 342, 333 and 317 nm in *n*-hexane. The absorption spectrum of compound 4 in *n*-hexane is given in Fig. S1 (supplementary information). This trend is observed in all the polar and non-polar solvents for compound 4. There is a good agreement between experimental absorption values and theoretical vertical excitation values. In DMF, the largest difference in wavelengths between the computed and experimental absorption maxima is 30 nm with 7.2% deviation.

The major intense absorption peaks in all the solvents can be assigned to HOMO to LUMO, HOMO to LUMO+1 and HOMO to LUMO+2 transitions of the R1 enol rotamer of compound 4. The frontier molecular orbital (FMO) 97 is the HOMO and FMO 98 is the LUMO for all the rotamers of compound 4 in all of the solvents. From the frontier orbital diagram (supplementary material, Fig. S3), the electron density of the HOMO is mainly concentrated on the phenyl ring and two 1,4-hydroxy groups attached to the phenyl ring and upon excitation, is redistributed onto the two benzothiazole rings in the LUMO. The two benzothiazole rings share more electron density in the LUMO state, so that these two rings act as an acceptor in the excited state and transfer of an acidic proton is promoted from the oxygen to basic nitrogen atoms. In chloroform the calculated vertical excitation for compound 4 is at 448 nm with an oscillator strength (f) of 0.6958, corresponding to a HOMO-LUMO electronic transition (98.7%) with the experimentally observed absorption being at 420 nm with a 6.7% deviation. The HOMO to LUMO+1 (97.7%) transition accounts for the vertical excitation at 354 nm with oscillator strength (f) 0.8389. This transition corresponds to the experimentally observed absorption peak at 341 nm with 3.8% deviation. A HOMO to LUMO+2 (95.3%) electronic transition is observed at 326 nm with oscillator strength (f) 0.1264. This transition corresponds to the experimentally obtained absorption peak at 321 nm with 1.6% deviation. In polar solvents, a similar trend is observed. This confirms that the experimentally observed short wavelength absorption in the range 317–321 nm is due to the HOMO to LUMO+2 excitation and that at 338–347 nm is due to the HOMO to LUMO+1 transition, whereas the longer wavelength absorption in the range of 426–414 nm is due to the HOMO–LUMO transition.

Solvent	Exper	imental	Theoretical					
	λ_{abs}	, λ _{em} nm	Vertical excitation			Emission		
	nm		nm (oscillator strength)	% Orbital contribution	%D	nm (oscillator strength)	%D	
n-Hexane	426	625	453 (R1-enol) H \rightarrow L (0.6085)	99.0	6.3	689 (R1-keto) L \rightarrow H (0.3153)	9.3	
	392	510				527 (R1-enol) L \rightarrow H (0.5397)	3.3	
	342	489	353 (R1-enol) H-1 → L (0.8780)	96.7	3.2			
	333							
	317		322 (R1-enol) H-2 \rightarrow L (0.1215)	95.3	1.6			
n-Heptane Chloroform	424	622	452 (R1-enol) H \rightarrow L (0.6125)	99.0	6.6	689 (R1-keto) L \rightarrow H (0.3174)	10.8	
	392	510				527 (R1-enol) L \rightarrow H (0.5437)	3.2	
	338	480	353 (R1-enol) H-1 \rightarrow L (0.8787)	96.7	4.4			
	329							
	317		321 (R1-enol) H-2 \rightarrow L (0.1218)	95.3	1.3			
Chloroform	420	617	448 (R1-enol) H \rightarrow L (0.6620)	98.7	6.7	674 (R1-keto) L → H (0.3463)	9.2	
	390	514				520 (R1-enol) L \rightarrow H (0.6140)	1.2	
	341	480	354 (R1-enol) H-1 \rightarrow L (0.8389)	97.7	3.8			
	334							
	321		326 (R1-enol) H-2 \rightarrow L (0.1264)	95.5	1.6			
Methanol	415	615	442 (R1-enol) H \rightarrow L (0.6589)	98.8	6.5	657 (R1-keto) L → H (0.3478)	6.8	
	389	516				512 (R1-enol) L \rightarrow H (0.6341)	0.8	
	343	474	352 (R1-enol) H-1 \rightarrow L (0.7878)	95.8	2.6			
	331							
	316		326 (R1-enol) H-2 \rightarrow L (0.1281)	95.2	3.2			
DMF	414	612	444 (R1-enol) H \rightarrow L (0.6876)	98.9	7.2	661 (R1-keto) L \rightarrow H (0.3625)	7.4	
	394	509				515 (R1-enol) L \rightarrow H (0.6627)	1.2	
	347	475	354 (R1-enol) H-1 → L (0.7983)	96.2	2.0			
	334							
	319		326 (R1-enol) H-2 \rightarrow L (0.1297)	95.4	2.2			

 Table 5
 Observed UV–Visible photo-physical data and computed photo-physical data for compound 4 in different solvents

Solvent	Exper	imental	Theoretical					
	λ_{abs}	λ _{em} nm	Vertical excitation			Emission		
	nm		nm (oscillator strength)	% Orbital contribution	%D	nm (oscillator strength)	%D	
DMSO	414	610	443 (R1-enol) H \rightarrow L (0.6851)	98.9	7.0	661 (R1-keto) L \rightarrow H (0.3613)	8.4	
	392	508				514 (R1-enol) L \rightarrow H (0.6611)	1.2	
	345	475	353 (R1-enol) H-1 \rightarrow L (0.7956)	96.1	2.3			
	331							
	318		326 (R1-enol) H-2 \rightarrow L (0.1296)	95.4	2.5			

Table 5 continued

The solvatofluorism study of compound 4 reveals the presence of two major emission peaks in all of the polar and non-polar solvents. The emission spectrum of compound 4 in *n*-hexane is given in the supplementary material (Fig. S2). The overlay of the experimental absorption spectrum and vertical excitation of compound 4 in *n*-hexane is given in Fig. S7 of the supplementary material. The long wavelength emission in all ESIPT molecules is due to the excited state keto tautomer obtained from the migration of the acidic proton to a basic nitrogen atom in the excited enol state. The transfer of the acidic proton is due to extra stabilization of the keto tautomer in the excited state compared with the excited enol tautomer, which is confirmed by the computations. The energy of the excited keto state obtained from TD-DFT calculations is lower than the corresponding excited enol state in solvents; this suggests that the stabilization is intrinsic. TD-DFT calculations suggest that the longer wavelength emission in the range 606–631 nm is due to a LUMO-HOMO transition from excited state keto* to ground state keto in all solvents, which corresponds with the observed emissions in the range 610-625 nm with 10.8% of maximum deviation. Usually, in the case of ESIPT compounds a single shorter wavelength emission in polar solvents is observed, attributed to a LUMO-HOMO transition from the excited state enol* to the ground state enol, implying the exclusive presence of an enol state. But, for compound 4, a longer wavelength emission is also observed in polar solvents irrespective of their polarity. The existence of this longer wavelength emission suggests the presence of a keto tautomer in polar solvents, which is further confirmed by the lower energies of the excited state keto conformers over their respective excited state enol conformer. The second emission of compound 4 in the range of 472-483 nm in different solvents corresponds to a LUMO–HOMO transition from an excited state enol* to the ground state enol, which corresponds to the observed emission in the range of 510–516 nm with maximum deviation of 3.2%; the third observed emission in the range of 475–489 nm may be a vibronic emission from the enol excited state to the enol ground state.

Compound 5 shows blue shifts in the absorption maxima and emission maxima in all the solvents compared with compound 4. Compound 5 shows only three prominent absorption peaks in comparison with compound 4, where 5 absorption peaks are observed in all the solvents. In *n*-hexane it shows absorption maxima at 404 nm, 371 nm and 322 nm. The absorption and emission spectra of compound 5 in *n*-hexane are given in the supplementary material (Figs. S4 and S5, respectively), the overlay spectra of observed absorption and vertical excitation of compound 5 in *n*-hexane are given in Fig. S8. The theoretical values of absorption

Solvent	Experimental		Theoretical					
	λ_{abs}	_{abs} λ _{em} m nm	Vertical excitation			Emission		
	nm		nm (oscillator strength)	Orbital contribution	% D	nm (oscillator strength)	% D	
<i>n</i> -Hexane	404	571	421 (R16-enol) H \rightarrow L (0.8820)	98.4	4.20	592 (R16-keto) L \rightarrow H (0.4127)	3.6	
	371	449	354 (R16-enol) H-1 \rightarrow L (0.5669)	95.7	4.6	476 (R16-enol) L \rightarrow H (0.8708)	6.0	
	322	420	341 (R16-enol) H-2 \rightarrow L (0.0295)	96.7	5.9			
<i>n</i> -Heptane	404	571	422 (R16-enol) H \rightarrow L (0.8863)	98.4	4.5	592 (R16-keto) L \rightarrow H (0.4186)	3.6	
	372	448	354 (R16-enol) H-1 \rightarrow L (0.5678)	95.7	4.8	476 (R16-enol) L \rightarrow H (0.8767)	6.3	
	320	421	341 (R16-enol) H-2 \rightarrow L (0.0294)	96.7	6.5			
Chloroform	400	575	423 (R16-enol) H \rightarrow L (0.9014)	98.5	5.8	596 (R16-keto) L \rightarrow H (0.4263)	3.6	
	361	452	353 (R16-enol) H-1 \rightarrow L (0.5958)	95.6	2.2	480 (R16-enol) L \rightarrow H (0.9529)	6.2	
	317	418	339 (R16-enol) H-2 \rightarrow L (0.0266)	96.5	6.9			
Methanol	395	578	420 (R16-enol) H \rightarrow L (0.8604)	98.2	6.3	600 (R16-keto) L \rightarrow H (0.4330)	3.8	
	361	457	351 (R16-enol) H-1 \rightarrow L (0.6092)	95.3	2.8	478 (R16-enol) L \rightarrow H (0.9470)	4.6	
	315	416	337 (R16-enol) H-2 \rightarrow L (0.0229)	96.4	6.9			
DMF	391	581	423 (R16-enol) H \rightarrow L (0.8955)	98.4	8.2	604 (R16-keto) L \rightarrow H (0.4396)	3.9	
	355	457	352 (R16-enol) H-1 \rightarrow L (0.6120)	95.5	0.8	482 (R16-enol) L \rightarrow H (0.9864)	5.5	
	314	415	337 (R16-enol) H-2 \rightarrow L (0.0238)	96.4	7.3			
DMSO	389	583	422 (R16-knol) H \rightarrow L (0.8912)	98.4	8.4	605 (R16-keto) L \rightarrow H (0.3407)	3.8	
	355	459	352 (R16-enol) H-1 \rightarrow L (0.6121)	95.5	0.8	481 (R16-enol) L \rightarrow H (0.9829)	4.8	
	313	414	337 (R16-enol) H-2 \rightarrow L (0.0236)	96.4	7.6	、 /		

Table 6 Observed and computed UV-visible photo-physical data of compound 5 in different solvents

show very good agreement with the observed values in all solvents. The maximum deviation in the theoretical vertical excitation from observed value is 8.4% in DMSO. In all the solvents, for compound 5, the major intense absorption peaks can be assigned to HOMO to LUMO, HOMO to LUMO+1 and HOMO to LUMO+2 transitions of the R16-enol rotamer, which is the thermodynamically most stable rotamer. The frontier molecular orbital (FMO) 101 is HOMO and FMO 102 is LUMO for all the rotamers in all the solvents. The two benzothiazole rings act as acceptors that, upon excitation, undergo HOMO to LUMO to LUMO transitions. The electron density

is mainly distributed on the phenyl ring along with the hydroxyl and methoxy groups attached to the phenyl ring in the HOMO that, upon excitation, redistribute the electron density on the two benzothiazole rings that are in one plane in the excited state.

Compound 5 in chloroform shows a HOMO–LUMO electronic transition (98.5%) for vertical excitation at 423 nm with oscillator strength (f) 0.9014. This vertical transition corresponds to the experimentally observed absorption at 400 nm with a 5.8% deviation. The HOMO to LUMO+1 (95.6%) transition corresponds to the vertical excitation at 361 nm with oscillator strength (f) 0.5959, which corresponds to the experimentally observed absorption peak at 361 nm with a 2.2% deviation, while the HOMO to LUMO+2 (96.5%) electronic transition appears at 339 nm, with oscillator strength (f) 0.0266 that corresponds to experimentally observed absorption peak at 317 nm with a 6.9% deviation. The orbital diagram for compound 5 is given in the supplementary material (Fig. S6). Also, in the case of polar solvents a similar trend is observed. This confirms that the experimentally observed short wavelength absorption in the range of 313–322 nm is due to the HOMO to LUMO+2 and at 355–372 nm is due to HOMO to LUMO+1 transition, whereas the longer wavelength absorption in the range of 389–404 nm is due to a HOMO–LUMO transition.

The solvatofluorism study of compound 5 shows three emissions peaks in all polar and non-polar solvents. The longer wavelength emission results from migration of an acidic proton to the basic nitrogen atom, which leads to enol-keto tautomerism. The migration of a proton for compound 5 occurs due to extra stabilization of the keto tautomer in the excited state compared to the excited enol tautomer, which is confirmed by computational calculations. Compound 5 shows a red shift in emission in going from non-polar to polar solvents. The longer wavelength emission in the range 592-605 nm is due to a LUMO-HOMO transition from the excited state keto* to ground state keto in all the solvents, which corresponds to the observed emissions range 571-583 nm with a 3.9% maximum deviation. The presence of longer wavelength emission in compound 5 in all polar and non-polar solvents shows a blue shift in comparison with the corresponding emissions shown by compound 4. Usually ESIPT compounds show a single shorter wavelength emission in polar solvents attributing to the LUMO-HOMO transition from excited state enol* to ground state enol suggesting the exclusive presence of the enol state. In case of compound 5, as for compound 4, a longer wavelength emission is also observed in polar solvents irrespective of their polarity. This indicates the presence of the keto tautomer in polar solvents, which is confirmed by the lower energies of excited state keto conformers over their respective excited state enol conformers. The second observed emission of compound 5 in the range of 449-459 nm resembles the transition from LUMO–HOMO for excited state enol* to ground state enol. This transition shows the theoretical emission is in the range of 476–482 nm with maximum deviation of 6.3%, whereas the third emission obtained is in the range of 421-414 nm and is associated with a vibronic transition from enol excited state to enol ground state.

4 Conclusions

In this paper we report the results of DFT and TD-DFT studies of 2,5-bis(2-benzothiazolyl)hydroquinone and 2,5-bis(benzo[d]thiazol-2-yl)-4-methoxyphenol. The structural parameters of the most stable conformers of 2,5-bis(2-benzothiazolyl)hydroquinone and 2,5-bis(benzo[d]thiazol-2-yl)-4-methoxyphenol were obtained by optimizing all of the possible conformers. The photo-physical behavior of these compounds was studied in six different solvents. The vertical excitation and emission wavelengths determined by using Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT) show very good agreement with observed absorption/emission values. The photophysical properties of the compounds are sensitive to the solvent's environment. Compound 4 shows a red shift in absorption and emission in comparison with compound 5.

Acknowledgements The authors thank the anonymous reviewers for their useful comments for improving the manuscript. M.M.J. is grateful to DST and TEQIP for financial support. L.R. and P.R. acknowledge the facilities from the University of Mauritius. I.A.A. and P.R. extend their appreciation to the International Scientific Partnership Program ISPP at King Saud University for funding this research work through ISPP# 0070.

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