5888 J. Phys. Chem. A 2009, 113, 5888–5895

Understanding Solvent Effects on Luminescent Properties of a Triple Fluorescent ESIPT Compound and Application for White Light Emission

Wenhao Sun, Shayu Li,* Rui Hu, Yan Qian, Shuangqing Wang, and Guoqiang Yang*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Received: January 23, 2009; Revised Manuscript Received: March 18, 2009

A triple fluorescent compound, *N*-salicylidene-3-hydroxy-4-(benzo[*d*]thiazol-2-yl)phenylamine (SalHBP), was dispersed in solid polymers and was developed as a white-light-emitting source in LED by using it as the first simple single compound with different configurations. The CIE coordinates were at (0.29, 0.35), close to those of pure white light. To explore speciation mechanisms in this single compound white light, SalHBP was dissolved in protic, nonpolar, and moderate polar solvent, respectively. Upon excitation, blue, green, and yellowish green emissions were observed from the three solutions at various temperatures. The conformation of SalHBP at room temperature was described by a Car−Parrinello molecular dynamics simulation. With the aid of hybrid density functional theory at the B3LYP/TZVP and PBE0/TZVP levels, three observed emission bands of SalHBP were assigned from the five most probable excited state conformations that were derived from four ground state conformations. The effect of solvent on the emission of SalHBP was summarized as a possibility for forming intermolecular hydrogen bonds between solvent and SalHBP molecules and competition between intra- and intermolecular hydrogen bonds.

Introduction

White-light-emitting organic materials have been attracting much research interest due to their important potential as solid state light sources such as flat panel displays and illuminations.[1] White light can be classified into two major types according to luminescent range: pure white light covers the whole visible energy region from 1.6 to 3.1 eV, and pseudowhite light (2.0 eV−3.1 eV) has no red light source.[2] Up to now, because of the limitation of intrinsic photophysical properties of organic molecules, it has been difficult to find a single chromophore that produces photon covering such a wide energy range whether it was pure white or pseudowhite light.[3] To compose white luminescence, as far as known, the most facile method is simply to mix several compounds with different emitting colors.[4] This strategy makes it difficult to control long-term color balance of white luminescence due to different stabilities for different compounds. For the improvement of color balance, several groups developed some methods and technologies, such as a single component polymer with copolymerizations of multiple chromophores, a single component organic compound nonconjugatedly linked with a multiunit of different emitting colors, fabrication of compounds with local and excimer/exciplex emission,[5] etc. These approaches have been successful in fabricating devices with white light emission. Meanwhile these methods also introduced more or less disadvantages, such as complicated procedures, high cost, or low stability.

Excited state intramolecular proton transfer (ESIPT) compounds are a class of potential illuminant materials. Several ESIPT compounds have been applied in some optic/optoelectrics devices, such as radiation hard-scintillator counters,[6] tunable solid state lasers,[7] and organic light emitting devices (OLEDs).[8] The ESIPT process is of great scientific and technological interest, and has been describe in detail with the help of some experimental and theoretical investigations.[9] The general accepted mechanism is that the ESIPT process incorporates a fast ($k \approx 10^{12}$ s^{-1}) excited state proton transfer from a proton donor to an acceptor group mediated by an intramolecular hydrogen bond (H-bond). A fast four-level photophysical cycle occurs immediately after photoexcitation.[10] Since the proton transfer tautomer is less stable in the ground state, it will transform to the initial tautomer with a ground state intramolecular proton transfer (GSIPT) process. It is noted that the ultrafast ESIPT process decreases intensively the probability of photochemical reactions for excited molecules, which enhances greatly the photostability of the molecules. From the spectroscopic point of view, for the ESIPT state, an emission gives abnormally large Stokes shift and no self-absorption is detected, even in the solution with relatively higher concentration. For their good photostability and no self-absorption properties, ESIPT compounds are expected to be potential intrinsic luminescent materials.

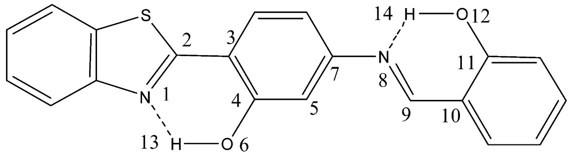
Moreover, since the process could be inhibited by an intermolecular H-bond formed with solvent molecules, the ESIPT is microenvironmentally sensitive. Thus the emission characteristics of ESIPT compounds are expected to be microenvironment dependent.[11] Some ESIPT compounds such as 2-(2′-hydroxyphenyl)benzoxazole (HBO) may exhibit dual luminescence bands (blue and green emission) that can be adjusted with various solvents or even circumambient pressure, temperature conditions.[12] Besides, a recent discovery in our group shows that a triple-luminescent ESIPT compound (SalHBP, shown in Scheme 1) may give rise to a nearly white emission, simultaneously emitting blue, green, and yellow light under high pressure.[13] So the tunable multiband emission property of luminescent ESIPT compound provides a possible route for fabricating a white-light-emitting source with a single-component luminescent material.

---

* To whom correspondence should be addressed. G.Y.: phone 86-10-62562693, fax 86-10-62562693, e-mail gqyang@iccas.ac.cn. S.L.: phone 86-10-82617263, fax 86-10-82617315, e-mail shayuli@iccas.ac.cn.

10.1021/jp900688h CCC: $40.75

SCHEME 1: Structure of SalHBP (intra-intra EE)



In the present work, application of SalHBP in polymer solvent as a solid state white light source was reported. As we observed, the color of the light source could be adjusted simply by changing the solid solvent of SalHBP. To understand this phenomena, some photophysical properties of SalHBP in three representative solvents were studied. We found that SalHBP exhibits blue, green, and yellowish green emission respectively in protic, nonpolar, and moderately polar solvent. With the help of correlated photophysical measurements and theoretical studies, the triple-color emissions were assigned from three excited state tautomers with a total of five represented structures—a local one and four ESIPT species belonging to a type of molecule.

Experimental Section

Materials. *N*-Salicylidene-3-hydroxy-4-(benzo[*d*]thiazol-2-yl)phenylamine (SalHBP) was synthesized according to the routines described in ref 13.

The copolymer (HEMA-VP) of 2-hydroxyethyl methacrylate (HEMA) and *N*-vinyl-2-pyrrolidone (VP) was prepared by a free-radical polymerization process.

Ethanol, 2-methyltetrahydrofuran (meTHF), dichloromethane, and methylcyclohexane (MCH) were AR grade from ACROS. Methanol was from DIKMA (HPLC grade). Polystyrene (PS) and polymethylmethacrylate (PMMA) were obtained from ACROS.

SalHBP and polymer (1:100, w/w) were dissolved in ethanol (for P(HEMA-VP)) or dichloromethane (for PS and PMMA). The resulting solution was applied to a commercial UV-LED set to form a covered film for light demonstration.

Ambient Spectra Measurements. The UV−visible absorption spectra of SalHBP dispersing in various solvents were recorded with a Hitachi U-3010 spectrophotometer. The steady state fluorescence spectra were measured by a Hitachi F-4500 spectrometer with excitation wavelength at 355 nm. The LED emission spectra were collected by a photomultiplier (ACTON 300i) with a spectral sensitivity correction determined by using a tungsten halogen lamp. The CIE coordinates have been calculated by using 1931 observer parameters.

Low-Temperature Spectra Measurements. Low temperatures were achieved with use of nitrogen-flow cryostats (Oxford OptistatDN). The temperature was controlled with a precision of 0.1 K with Oxford ITC503 temperature controllers. The emission spectra were recorded with an Edinburgh FLS920 spectrometer, using an excitation wavelength of 355 nm.

Computational Methods. Geometry optimization for the ground state of the SalHBP molecule were carried out by using the GAUSSIAN 03 software package[14] with the density functional theory. Becke's three-parameters hybrid method, using the Lee−Yang−Parr correlation functional (B3LYP), was employed here. Structures of the lowest excited state tautomers for SalHBP were obtained by TDDFT (time-dependent density-functional theory) methods, using the TURBOMOLE suite,[15] employing the hybrid functional PBE0. The geometries were fully optimized without symmetry constraints. On the basis of ground and excited state optimization, TDDFT was applied to investigate the excited state electronic properties of SalHBP. All calculations above employed the TZVP basis set for carbon, hydrogen, oxygen, nitrogen, and sulfur atoms.

Car−Parrinello molecular dynamics were carried with use of the CPMD 3.11 code[16] for studying two intramolecular hydrogen bonds in SalHBP. The KS equations were solved by using the Becke−Lee−Yang−Parr functional and plane-wave basis set up to 25 Ry cutoff energy. Core electrons were taken into account through the use of Vanderbilt's ultrasoft pseudopotentials.[17] The time step for integrating the equations of motion was 0.06 fs, and the fictitious electronic mass was set to 400 au. The temperature of the SalHBP molecule was kept at 300 ± 30 K by a Nosé−Hoover chain at a frequency of 3000 cm^{-1}. The system included a cubic cell that contained a sole SalHBP molecule without periodic boundary conditions. The starting configuration was extracted from optimized geometry, and then simulation was carried out for 16.7 ps.

Results and Discussion

Figure 1 showed the colorful emission from SalHBP dispersed in copolymer (mole ratio of HEMA:VP = 3:7), PS, and PMMA. A commercial LED (365−375 nm) illuminated weak blue light. A thin transparent polymer layer from an ethanol (for HEMA-VP copolymer) or dichloromethane (for PS and PMMA) solution was coated onto the LED head. Upon illumination, these LEDs generated white light, bluish green light, and yellowish green light, respectively. On the chromaticity diagram, these emissions showed CIE coordinates at (0.29, 0.35), (0.26, 0.38), and (0.30, 0.42), in which the white emission was close to that of pure white light (0.33, 0.33). Apparently, SalHBP can be considered as a potential material for single-component pseudowhite light application.

To understand deeply the white light emission, in the following section, photophysical properties of SalHBP in various solvents and factors for solvent-dependent emission were discussed.

Optical Absorption and Photoluminescent Spectra in Ambient Condition. Solid SalHBP is an orange crystal at room temperature and it is soluble in all conventional organic solvents. Figure 2a showed the absorption spectra of SalHBP in MCH, meTHF, and methanol at room temperature. SalHBP exhibited an absorption peak at ∼370 nm in three organic solvent, which could be assigned to the $\pi-\pi^*$ transition of the molecule. The absorbance of SalHBP showed no obvious change with an increase in the polarity of solvent. Because ESIPT compounds could form intermolecular H-bonds with protic or strong polar solvent, the ground state structure of SalHBP molecules could be diverse. A small change of the absorption spectrum in different solvents indicated only that the dye molecule had no apparent conjugation−structural changes in the ground state in different solvents. The assignment of absorbance for SalHBP will be discussed in a later section about ground state geometries and conformations.

The fluorescence spectra of SalHBP in various solvents were shown in Figure 2b. Unlike the case of absorbance in the solvents, SalHBP exhibited a significant change in both fluorescence shape and intensity with increasing polarity of solvent, which was similar to those of some other ESIPT compounds dissolved in liquid solvent.[12b,18] In meTHF solution, SalHBP showed two peaks with maxima at ∼416 and ∼538 nm, respectively, but only one emission band at ∼538 nm was observed in MCH solution. Similarly, SalHBP also exhibited two emission bands in protic solvent−methanol, ∼416 and ∼538 nm, respectively. But the emission in the high-energy

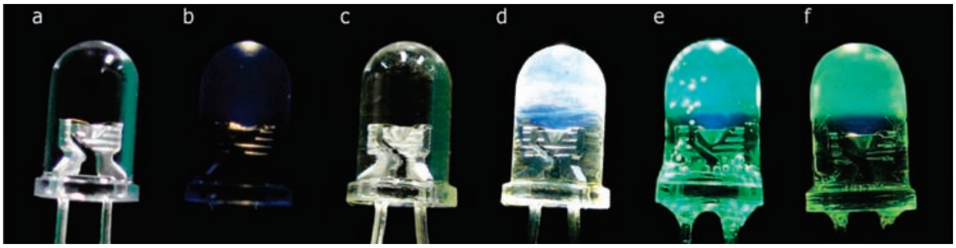


Figure 1. Photos of (a) a reference UV LED (365−375 nm) without illumination, (b) the illuminating reference LED, (c) the same LED coated with a thin layer of SalHBP HEMA-VP copolymer solution without illumination, (d) the illuminating LED shown in part c, (e) the same LED illuminating a coated thin layer of SalHBP PS solution, and (f) the same LED illuminating a coated thin layer of SalHBP PMMA solution.

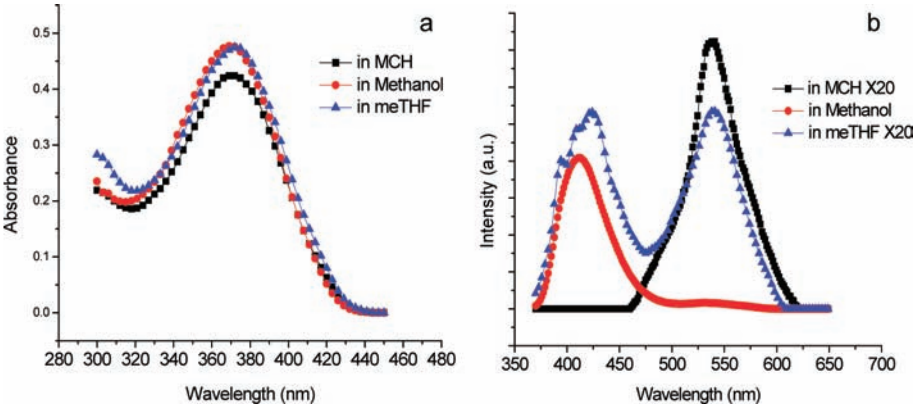


Figure 2. UV−vis absorption spectra (left) and normalized fluorescence emission spectra (right) of SalHBP (1.0×10^{-5} M in molecule) in various solvents at room temperature. Emissions in MCH and meTHF have been multiplied by 20-fold, respectively. Excitation wavelength: 355 nm.

area increased more than 1 order of magnitude compared to that of the meTHF solution.

Additionally, the fluorescence spectra of the SalHBP in alcoholic solvent, MCH, and meTHF were measured at lower temperature (in steps of 20 deg from 280 to 140 K) and shown in Figure 3. With decreasing the temperature, the fluorescent intensities of SalHBP in the three solvents presented a monotonous enhancement. The locations of the emission were almost unchanged while there were some differences in spectral shapes from different solvents. In an alcoholic mixture, the main emission band was around 410 nm and it was enhanced only about 4-fold from 280 to 140 K. Moreover, a remarkable increase of a weak emission band at ~500 nm was observed when the temperature was below 180 K. Meanwhile, at lower temperatures, the fine structure of the emission band around 410 nm was detected, two shoulders at 430 and 450 nm were clear in the spectra. From an observable point of view, the SalHBP alcoholic solution presented apparent blue emission over the whole measured temperature range, which was besides a few cyan characters at lower temperature. In nonpolar MCH solution, SalHBP exhibited only a wide broad (fwhm = 108 nm) emission band with a maximum at 495 nm. With a temperature decrease from 280 to 140 K, the intensity of the emission was increased by almost 28-fold. The solution produced bright green emission, which could be observed with the naked eyes. Besides, inconspicuous fine structure of emission spectra was observed at 140 K. In the case of meTHF solution, SalHBP exhibited an emission band with a peak at about 538 nm. And two weak shoulders were observed at around 420 and 500 nm, respectively. At 140 K, SalHBP solution emitted a brilliant yellowish-green light with a few white light characteristics for its blue light component. As observed above, SalHBP could emit blue (CIE1931 0.20, 0.16) in methanol/ethanol, green (CIE1931 0.32, 0.46) in MCH, and yellowish-green (CIE1931 0.33, 0.42) in meTHF without obvious temperature-dependent color changes.

To directly compare the emission of SalHBP in different solvents, the normalized fluorescent spectra were given in Figure 3D. It was obvious that all three spectra were composed of several (at least three) emission bands located at about 420, 490, and 538 nm. In our previous work, the three emission bands were presumed to come separately from excited state EE, KE, and EK tautomers.[13] This assignment will be discussed in a later section about the lowest excited state geometries. As known, electrostatic and hydrogen bonding were the main types of solvent−solute interactions.[19] Considering the fact that locations of the three emission bands showed no apparent shifts in different solvents, we suggested that the solvent did not have an apparent effect on the electronic configuration of the excited state SalHBP molecules, but influenced heavily the population of the three excited state tautomers. Furthermore, the latter was interrelated closely to the population of the ground state conformation.

In the following sections, the possible tautomer geometries (both in the ground and excited state) of the SalHBP molecule in different solvents will be discussed, and finally the solvent-dependent emission will be explained.

Conformation of Ground State SalHBP in Various Solvents. As known, ESIPT was a very fast reaction route (k_{ESIPT} is usually $\sim 10^{12}$ s^{-1}) compared with the radiation process ($k_r \approx 10^8$ s^{-1}).[20] Thus, if the ESIPT reaction proceeded, the emission from the enol form would not be observed anymore. However, the intramolecular H-bond could be dissociated by surrounding the H-bond donor and/or acceptor. In this case, the ESIPT from enol to keto could be prohibited by the solvent molecules. Therefore, ESIPT emission would be the predominant fraction when the dyes were dispersed in nonpolar solvent that did not influence the proton-transfer reaction. When the protic solvents caused hindrance of the intramolecular H-bond, the short-wavelength emission from the enol tautomer was the major part of the luminescence. As in other polar solvents without a protic group, the emission of the dyes was determined by competition

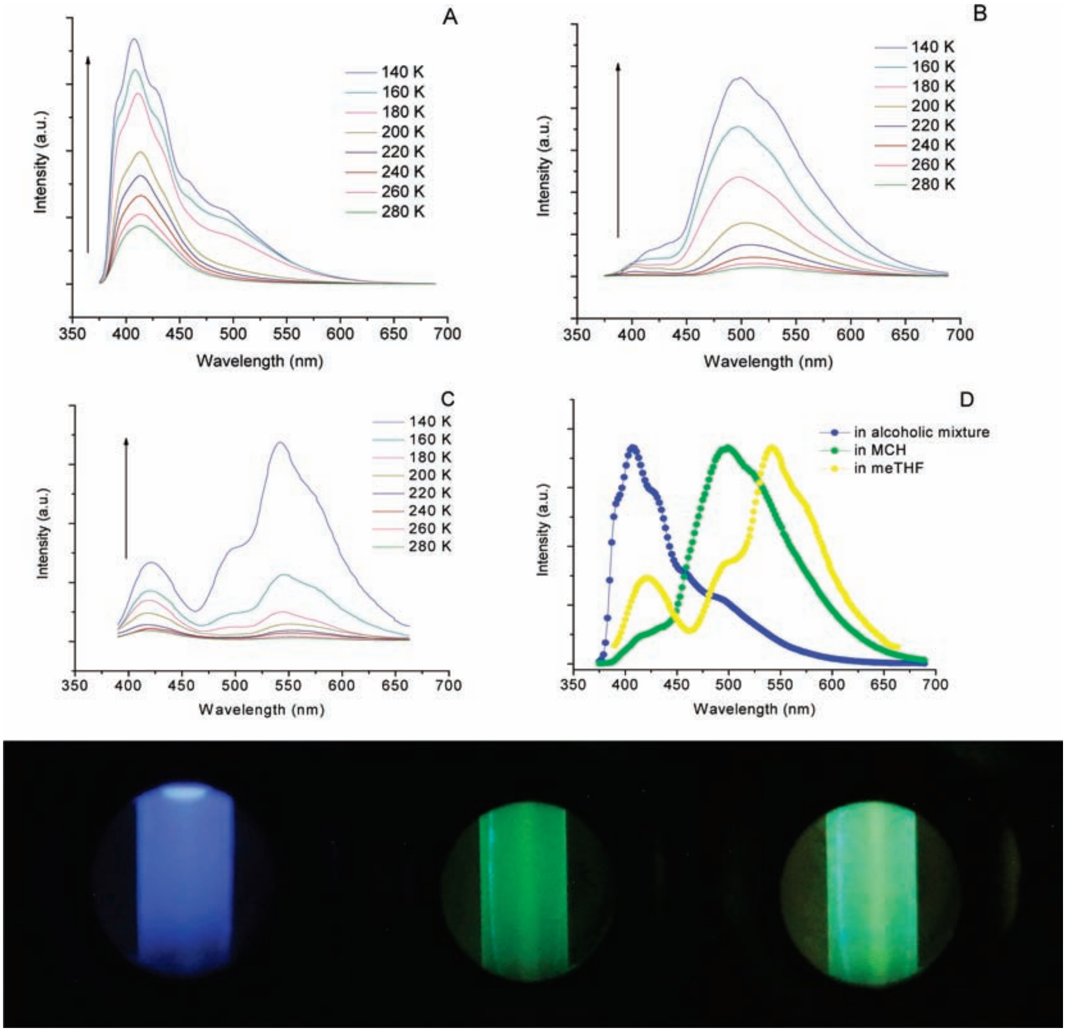


Figure 3. Emission spectra of SalHBP (1.0×10^{-5} mol/L) at various temperatures: (A) in alcoholic solvent (v/v methanol:ethanol = 4:1); (B) in MCH; (C) in meTHF; and (D) the normalized fluorescent spectra at 140 K. Excitation wavelength: 355 nm. Bottom: Photos of SalHBP emission in alcoholic solvent (left), MCH (middle), and meTHF (right) at 140 K. Note: Panel C was reproduced with permission from ref 13. Copyright 2007 American Chemical Society.

between inter- and intramolecular H-bonds. This was a generally accepted mechanism for luminescence of ESIPT compounds in different solvents.[21] But in our case, it was more complicated. For SalHBP, there were two possible H-bonds for its chemical structure. Although the three tautomers were shown as saturated intramolecular H-bond forms in our previous work, conformations with a full or partial intermolecular H-bond could probably exist in different solvents. To distinguish the strength of two intramolecular H-bonds (N1···H13 and N8···H14 shown in Scheme 1), Car−Parrinello molecular dynamics (CPMD) NVT simulations were performed for the ground state SalHBP. The calculation was set to the isolated system to limit computer resources.

Figure 4 contained the two possible H-bond distances as a function of time with mean and standard deviation values for the trajectory. The distance of N1···H13 fluctuated for the most part between a higher value of 235 pm and a lower value of 136 pm, suggesting an intramolecular H-bond form. The exceptionally high value of 285 pm meant bond breaking of the intramolecular H-bond and implied a possibility of intermolecular H-bond formation. Similar behavior was observed in the case of N8···H14. In total simulation time, the highest and the lowest values of distance observed were 256 and 129 pm, respectively, which was slightly larger than that of N1···H13. From Figure 3 it could be seen that the mean of two H-bond distances was almost the same. This suggested that the difference of the two H-bonds was very small. The distribution of two distances of N1···H13 and N8···H14 was also shown in Figure 4. The smaller value of maximum count and lager fwhm of N8···H14 indicated that the intramolecular H-bond of N8···H14 was weaker than that of N1···H13, but actually, the difference was very small. It was rational to assume that the broken probability of the two intramolecular H-bonds was very similar and thus the possibility for forming an intermolecular H-bond with solvent molecules was similar.

Another important factor for molecular conformation was rotation of a single bond. There were three single bonds in the conjugation system of SalHBP: C2−C3, C7−N8, and C9−C10. Figure 5 showed three dihedral angles involving the three single bonds as a function of time. It was obvious that the main fluctuation range of $\phi_{8-9-10-11}$ was about 30°, which was the smallest among the three dihedral angles, and its mean value was close to 0°. This suggested that the internal kinetic energy was not sufficient for easy rotation of the phenol group and thus the salicylidene subunit was stable and close to the planar conformation. As for the other two bonds, both of them were apparently fluctuant, with ranges as high as 60−70°. These computational results indicated no 360° rotation in conformation changes of SalHBP. This was not surprising to $\phi_{5-7-8-9}$ for the

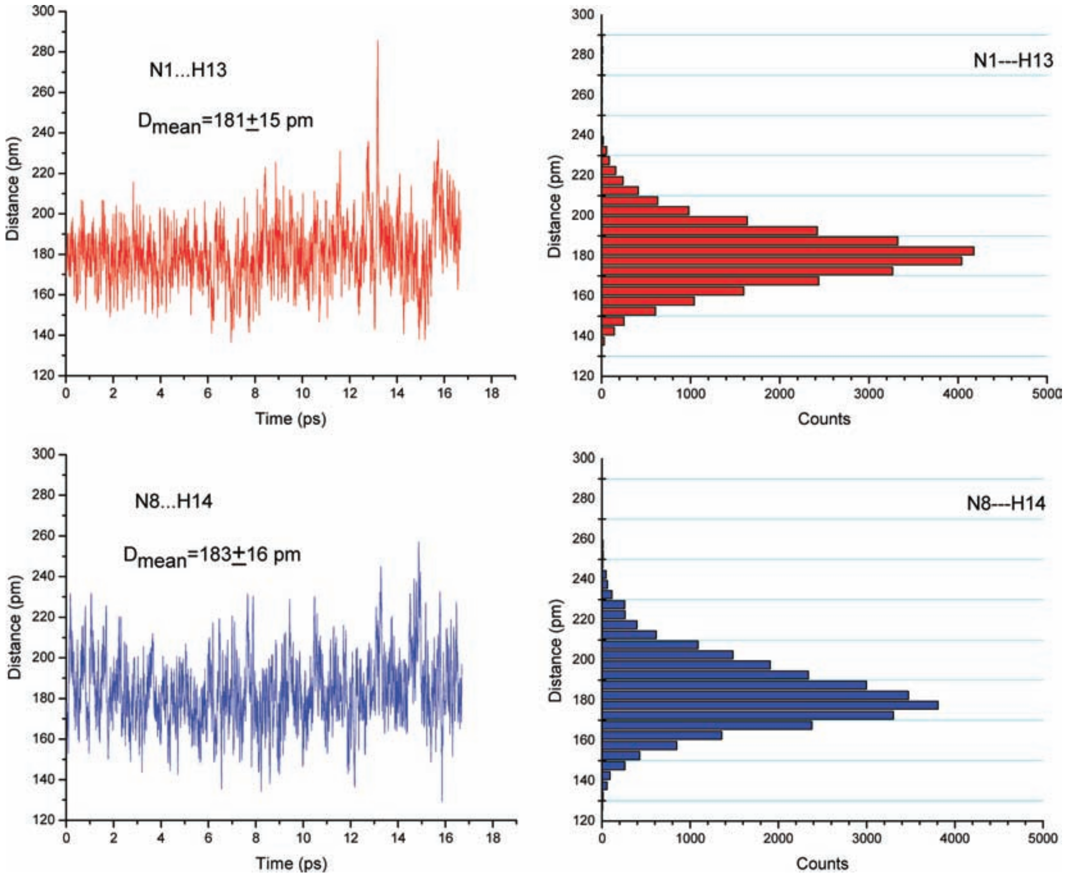


Figure 4. Two possible H-bond distances as a function of time (left) and distribution (right).

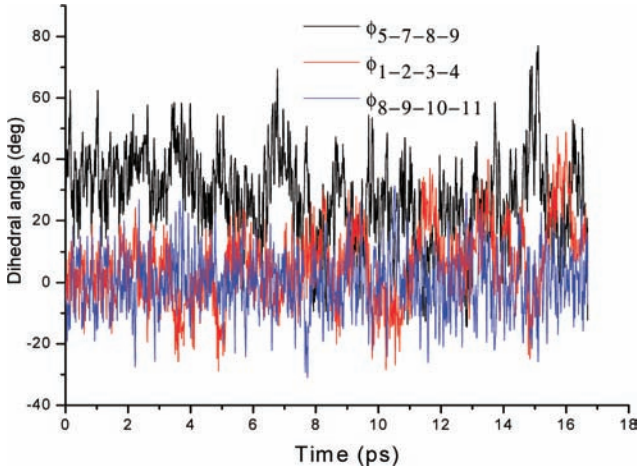


Figure 5. Three dihedral angles as a function of time.

block of two H atoms located in C6 and C9. As to $\phi_{1-2-3-4}$, this may be understood as the effect of the intramolecular H-bond.

On the basis of the molecular dynamics simulation above, the conformation of isolated ground state SalHBP could be depicted as follows. In main timeframe, SalHBP molecules exhibited a saturated intramolecular H-bond conformation (intra-intra EE as shown in Scheme 1) for the thermodynamicly favorable rule, and the single bond located in the conjugation system would not take a rotation motion that exceeded 90°. In this case, SalHBP was expected to present obvious ESIPT emission as excitation, which was also regarded as an explanation for the case that SalHBP was monodispersed in nonpolar solvent shown in Figure 3B. As SalHBP dissolved in protic solvent, solvent molecules showed a great possibility for breaking up intramolecular H-bonds of SalHBP and forming intermolecular H-bonds. Therefore, the major part of SalHBP molecules in protic solvent exhibited saturated intermolecular H-bond conformations, while a few molecules still had intramolecular H-bond conformations just as their emission shows in Figure 3A. It should be mentioned that the single bond C2−C3 would afford a rotation that exceeded 90° without hindrance of the H-bond N1−H13, which was similar to other 2-(2′-hydroxyphenyl)benzothiazole (HBT-type) compounds.[22] Thus, emission of SalHBP in protic solvent originated mainly from two intermolecular H-bond conformations shown in Scheme 2. As SalHBP dispersed in other polar solvents, competition between intra- and intermolecular H-bonds related closely to innate properties of the solvent molecules. In this case the ground state conformation of SalHBP was diversity. Inter-inter, intra-intra, inter-intra and intra-inter H-bond conformations were possible, and the population of these conformations was determined by the electronegativity of the atom in the solvent molecule.

On the basis of the CPMD simulations mentioned before, the probable conformations of SalHBP in various solvents were brought forward. As known, the basic emission properties for organic luminophor were strongly related to the characteristics of the low-lying excited electronic states and ground electronic states of the molecules. To gain insight into the emission phenomena, we did theoretical investigations to determine the most probable ground state and the lowest excited state conformations of SalHBP in various solvents.

The Most Probable Ground State Geometries of SalHBP and Excitation Energy Molecular Orbitals. As seen in the molecular structure (Scheme 1), SalHBP could be considered

SCHEME 2: Structures of Represented Conformations

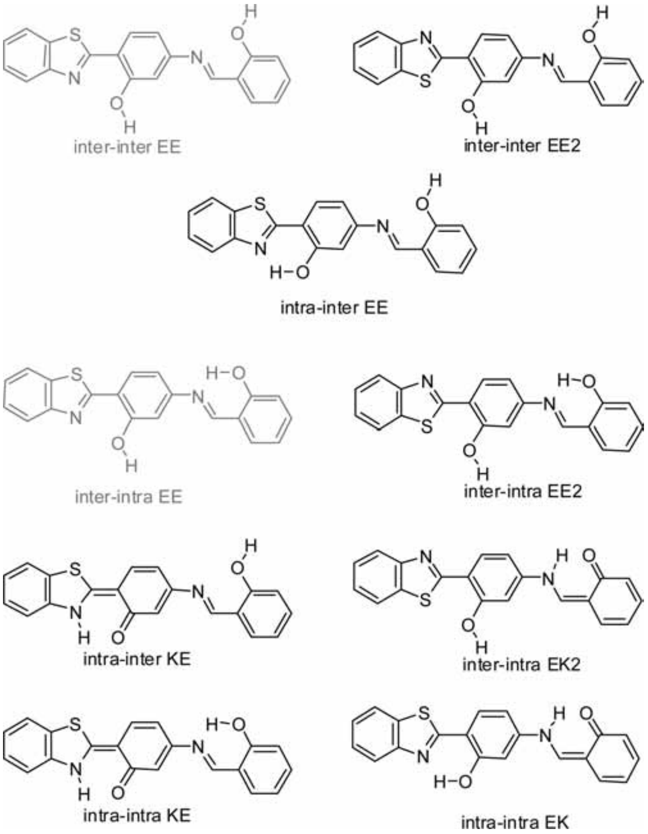


TABLE 1: The Calculated Vertical Excitation Energies (nm) of the Four Conformations for the EE Tautomer with Oscillator Strength in Parentheses

	HOMO → LUMO			
experiment	intra-intra EE	inter-inter EE2	intra-inter EE	inter-intra EE2
∼370	387 (1.007)	387 (0.807)	385 (0.851)	388 (1.016)

as a overlapping combination of 2-(2′-hydroxyphenyl)benzothiazole (HBT) and salicylideneaniline (SA).

When the molecules were dissolved in protic solvent, two intermolecular H-bonds could be formed as mentioned above. Therefore, structures of the inter-inter EE and EE2 tautomer were optimized by freezing $\phi_{3-4-6-13}$ and $\phi_{10-11-12-14}$ to 180°. The salicylidene subunit was still planar while the HBT subunit was no longer planar and exhibited torsion. The dihedral angles $\phi_{1-2-3-4}$ and $\phi_{5-7-8-9}$ were calculated as 29.0° and 42.8° for EE and 179.9° and 43.1° for EE2, respectively. Obviously, two subunits of the inter-inter EE tautomer were much less coupled than that in the intra-intra tautomer, which means a decrease in the conjugation degree of the whole molecule. The energy barrier from inter-inter EE to EE2 conformations was estimated to be 8.4 kJ/mol by fixing $\phi_{7-8-10-11}$ to 90°, which was the same order of magnitude as the average thermal motion energy of a molecule and possible to overcome through thermomotion. From the computational result, the energy of EE was about 16.1 kJ/mol higher than that of EE2; the inter-inter EE2 was seldom able to transform back to inter-inter EE and should be the predominant conformation of SalHBP in the ground state in protic solvent.

As dissolved in nonpolar solvent, two intramoleculer H-bonds of SalHBP exist for most of the time. In this case, both HBT subunit and Salicylidene subunit were completely planar for minimizing system energy. However, a dihedral angle between the two subunits was observed in DFT structures of SalHBP in the ground state, which was 34.8° for the intra-intra EE tautomer. The value of the dihedral angle was similar with that in SA. For SA, it was reported that the dihedral angle was 33.1° for the enol tautomer.[23] Additionally, the ground state structures of two proton-transfer tautomers were optimized for comparison. The computational ground state energies significantly depend on the configuration of the molecules. Compared to the intra-intra EE, the relative energy of intra-intra KE (40.0 kJ/mol) was much higher than that (14.0 kJ/mol) of the intra-intra EK structure, which could be induced by conjugation decreased due to the larger value of the dihedral angle for $\phi_{5-7-8-9}$ (KE:EK = 39.3° vs. 0°). The larger value of the relative ground state energy implied that the intra-intra KE tautomer was not possibile to populate in the ground state of SalHBP molecules. As for the intra-intra EK tautomer, a relatively smaller energy indicated that only a very few EK species could exist through molecular thermomotions, which was observed for several other SA-type compounds.[9b,24] Thus, computational results validated that most ground state molecules of SalHBP should be the intra-intra EE structure.

As dissolved in polar solvent, besides intra-intra EE and inter-inter EE conformations, intra-inter EE and inter-intra EE conformations of SalHBP were possible to be a large population. In the calculation, the optimization structure of the intra-inter EE conformation is similar to the structure of intra-intra EE. The dihedral angles $\phi_{1-2-3-4}$ and $\phi_{5-7-8-9}$ were calculated as 0° and 43.5°, respectively. For another case analogous to that of inter-inter EE, the inter-intra EE structure presented two conformations due to the rotation of benzothiazole as shown in Scheme 2. The energy barrier from inter-intra EE1 to EE2 was calculated as 8.2 kJ/mol and the energy of EE2 was about 16.3 kJ/mol lower than that of EE1. Thus, the stable conformation of the inter-intra EE structure was EE2.

In Table 1, we listed the vertical excitation energies of the most preferred conformations of the ground state calculated at the optimized structure, together with the oscillator strengths. The calculated energies with significant oscillator strengths were compared directly to the experimental absorption peaks. As mentioned above, monodispersal SalHBP exhibited only a wide absorbance with a peak at ∼370 nm. Considering the fact that the TDDFT method tended to underestimate the excitation energies,[25] we could assume that the calculated values corresponded well to the experimental spectra. It was interesting that the vertical excitation energies of these different conformations were almost identical, which agreed with the experimental results. Additionally, the large oscillator strength of the lowest energy transition for the EE tautomer also suggested that the major part of the absorption spectra originated from an electronic transition of various conformations of the EE structure. Furthermore, it was helpful to interpret the observed spectral features to calculate frontier molecular orbitals with shape description in detail. The shapes of all these orbitals for the four conformations were spread out over the whole molecule, which corresponded to molecular π and π^* orbitals. Thus, the absorption peak of SalHBP was assigned as a typical $\pi-\pi^*$ characteristic.

Lowest Excited Singlet State Geometries of SalHBP and Emission Energy. On the basis of the fact that the rate of ESIPT is much faster than that of other decay processes, the four most preferred EE conformations of the ground state would change finally to five excited state conformations after excitation. The intra-intra EE conformation would transform to the intra-intra

TABLE 2: The Calculated Vertical Transition Energies (nm) of the Five Excited State Conformations with Transition Dipole Moment (debye) in Parentheses

experiment	intra-intra KE	intra-intra EK	inter-inter EE2	intra-inter KE	inter-intra EK2
~410, ~500, ~538	503 (5.21)	526 (6.69)	427 (10.86)	501 (4.92)	507 (6.96)

KE and EK conformations shown in Scheme 2. The inter-inter EE2 would remain unchanged roughly. Intra-inter EE and inter-intra EE2 would convert correspondingly to the intra-inter KE and inter-intra EK2 tautomers shown in Scheme 2. The calculated emission energies of five excited state conformations and their dipole moment were listed in Table 2, which were consistent with the experimental data.

In protic solvent, the inter-inter EE2 was the main luminescent state. From the optimized geometry of the inter-inter EE2 excited state, the benzothiazole ring and the salicylidene subunit were not coplanar with the central phenol ring, and inclined in identical directions, through twists of 14.5° and 19.5°, respectively. The emission energy was calculated as 2.906 eV (427 nm), which would present a blue emission corresponding well to experiment. The calculated value exhibited a few red shifts compared to the experimental emission peak, which implied that the excited state molecule with less conjugation conformation was also luminescent.

In nonpolar solvent, intra-intra KE and EK conformations were the most preferred ones. From the optimized geometry of the intra-intra KE conformation at the lowest excited state, the whole molecule was almost planar and the dihedral angle $\phi_{5-7-8-9}$ was only 4.7° and the intramolecular H-bonds caused complete planarization of HBT and SA subunits. The calculated emission energy of the intra-intra KE conformation was 2.465 eV (503 nm). Besides, from the optimized excited state of the intra-intra EK conformation, the protonation of the N atom in the SA subunit and intramolecular H-bonds caused the molecule to be coplanar. Accordingly, there was a red shift in the emission of the EK conformation compared to the KE conformation, and the calculated emission energy was 2.357 eV (526 nm). The calculated results corresponded to the experimental data of SalHBP dissolved in MCH, as shown in Figure 3.

In polar solvent, however, besides the three excited state conformations mentioned above, intra-inter KE and inter-intra EK2 were also possible in great population. Unlike the intra-intra KE conformation, the optimized geometry of the intra-inter KE conformation was relatively nonplanar. The dihedral angle $\phi_{5-7-8-9}$ was 19.7°. Correspondingly, the emission energy of intra-inter KE was higher than that of intra-intra KE and was calculated as 2.475 eV (501 nm). As for the inter-intra EK2 conformation, the calculated geometry was also completely planar similar to that of the intra-intra EK conformation. Nevertheless the emission energy was higher than the full intra H-bond conformation and was calculated as 2.432 eV (510 nm).

We found a nice agreement between calculation and experiment, especially for those low-polarity conformations in the intermediate transition energy region. It was well-known that TDDFT may lead to quite wrong results when describing charge-transfer excited states.[26] In our cases, all S_1 excited states of those conformations except inter-inter EE2 showed unnoticeable charge separation so that calculations should provide an accurate description for the excited states. As for the inter-inter EE2 conformation, the relatively large deviation of calculation was understandable for its large polarity and without considering solvent effects.

On the basis of the calculation results of various lowest excited singlet state conformations, we predicted the emission of SalHBP in different solvents as follows: (1) in methanol, the blue emission was assigned from the excited state tautomer with inter-inter EE2 conformation, (2) in MCH, the green emission with a wide band was from both intra-intra KE and intra-intra EK conformations, and (3) in meTHF, the relatively high polarity of solvent increased the population of conformations with large excited state dipole moment, which induced the red shift of the main emission band compared to the case in MCH. By combining these luminescences with suitable proportion (i.e., controlled the population of various excited state conformations by adjusting the solvent), we obtain the pseudowhite light source with a single dye.

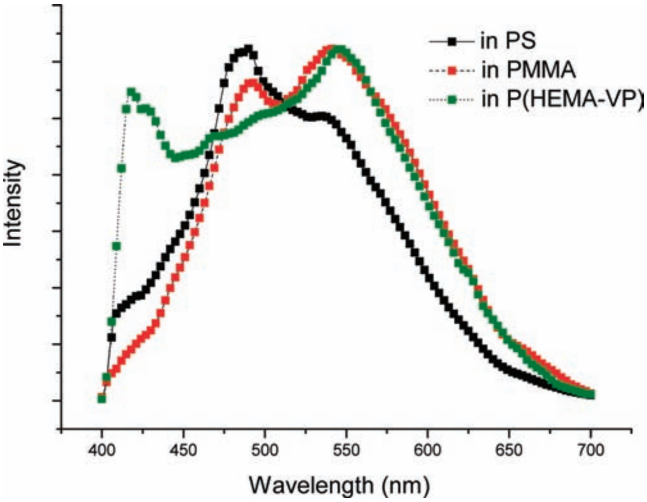


Figure 6. Photoluminescence of a UV LED coated with a thin layer of SalHBP polystyrene, PMMA, and HEMA-VP (molar ratio 3:7) copolymer solution (with a 400 nm cutoff filter).

Thus, the different emission color of coated LEDs shown in Figure 1 could be explained as follows. In PS, the case of SalHBP was similar to that in MCH mentioned before where two intramoleculer H-bonds of SalHBP exist most of the time, and the emission originated from two ESIPT excited state configurations and presented a green light for low polarity of PS. In PMMA, the possibility for forming intermolecular H-bonds between SalHBP and polymer was still low. But with higher polarity compared with MCH, PS, and meTHF, PMMA could increase the population of the tautomer with longer wavelength emission. So in PMMA, yellowish green light was observed upon illumination. As SalHBP dissolved in HEMA-VP copolymer, the case was more complicated. Figure 6 showed the photoluminescence spectrum of LED coated with SalHBP in HEMA-VP copolymer. It was obvious that the spectrum was similar to the simple overlap of three spectra shown in Figure 3D, even locations for every shoulder. This suggested that each excited state conformation with different luminescence mentioned above was populated in the copolymer, which was what we expected. This phenomenon was also explained by balance between intra- and intermolecular H-bonds. As we know, both HEMA and VP presented a great chance to form an intermolecular H-bond with dissolved molecules— in this case, SalHBP.[27,28] But the possibility decreased when monomer was polymerized to polymer for the limitation of free motion of the macromolecules. The suitable limitation resulted in a suitable population of conformations with different color emission. By tuning the ratio of HEMA to VP, the coated LED generated pseudowhite light that was a combination of all emissions from several conformations of SalHBP, covering the whole visible range from 400 to 700 nm.

Conclusions

With spectral measurements and computations, triple emission bands of SalHBP were assigned from five most probable excited state conformations, which originated from four most probable ground conformations with excitation. The results gave a novel route to understanding the effect of solvent polarity and ability for forming H-bonds of ESIPT compounds on emission color. On the basis of solvent-dependent and switchable blue/bluish green/greenish yellow fluorescence, SalHBP was designed to generate pseudowhite light in solid polymer. It was developed as a white-light LED source with the first simple single compound with different molecular configurations. The advantage for the single and simple dye-coated white LED makes it possible to overcome the color-cast problem for long-term application.

Acknowledgment. This research was supported by the National Natural Science Foundation of China (Grant Nos. 20703049, 20733007, 20573122, and 20873165) and the National Basic Research Program (2007CB808004).

References and Notes

(1) (a) Gong, X.; Wang, S.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2005**, *17*, 2053. (b) Xie, Z. Y.; Huang, J. S.; Li, C. N.; Liu, S. Y.; Wang, Y.; Li, Y. Q.; Shen, J. C. *Appl. Phys. Lett.* **1999**, *74*, 641. (c) Liu, Y.; Nishiura, M.; Wang, Y.; Hou, Z. M. *J. Am. Chem. Soc.* **2006**, *128*, 5592.

(2) (a) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1994**, *64*, 815. (b) Sun, H. Z.; Zhang, J. H.; Zhang, H.; Xuan, Y.; Wang, C. L.; Li, M. J.; Tian, Y.; Ning, Y.; Ma, D. G.; Yang, B.; Wang, Z. Y. *ChemPhysChem.* **2006**, *7*, 2492.

(3) Kim, S.; Seo, J.; Jung, H. K.; Kim, J. J.; Park, S. Y. *Adv. Mater.* **2005**, *17*, 2077.

(4) Strukelj, M.; Jordan, R. H.; Dodabalapur, A. *J. Am. Chem. Soc.* **1996**, *118*, 1213.

(5) (a) Yang, Y. J.; Lowry, M.; Schowalter, C. M.; Fakayode, S. O.; Escobedo, J. O.; Xu, X. Y.; Zhang, H. T.; Jensen, T. J.; Fronczek, F. R.; Warner, I. M.; Strongin, R. M. *J. Am. Chem. Soc.* **2006**, *128*, 14081. (b) Jiang, J. X.; Xu, Y. H.; Yang, W.; Guan, R.; Liu, Z. Q.; Zhen, H. Y.; Cao, Y. *Adv. Mater.* **2006**, *18*, 1769. (c) Wu, W. C.; Lee, W. Y.; Chen, W. C. *Macromol. Chem. Phys.* **2006**, *207*, 1131. (d) Tsai, M. L.; Liu, C. Y.; Hsu, M. A.; Chow, T. J. *Appl. Phys. Lett.* **2003**, *82*, 550. (e) Xu, Y. H.; Peng, J. B.; Mo, Y. Q.; Hou, Q.; Cao, Y. *Appl. Phys. Lett.* **2005**, *86*, 163502.

(6) Renschler, C. L.; Harrah, L. A. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1985**, *235*, 41.

(7) Sakai, K. I.; Tsuzuki, T.; Itoh, Y.; Ichikawa, M.; Taniguchi, Y. *Appl. Phys. Lett.* **2005**, *86*, 081103.

(8) Chang, S. M.; Tzeng, Y. J.; Wu, S. Y.; Li, K. Y.; Hsueh, K. L. *Thin Solid Films* **2005**, *477*, 38.

(9) (a) Kownacki, K.; Mordzinski, A.; Wilbrandt, R.; Grabowska, A. *Chem. Phys. Lett.* **1994**, *227*, 270. (b) Ziółek, M.; Kubicki, J.; Maciejewski, A.; Naskrecki, R.; Grabowska, A. *Chem. Phys. Lett.* **2003**, *369*, 80. (c) Zgierski, M. Z. *J. Chem. Phys.* **2001**, *115*, 8351.

(10) Qian, Y.; Li, S. Y.; Zhang, G. Q.; Wang, Q.; Wang, S. Q.; Xu, H. J.; Li, C. Z.; Li, Y.; Yang, G. Q. *J. Phys. Chem. B* **2007**, *111*, 5861.

(11) (a) Joshi, H.; Kamounah, F. S.; Gooijer, C.; Van der Zwan, G.; Antonov, L. *J. Photochem. Photobiol. A* **2002**, *152*, 183. (b) Ohshima, A.; Momotake, A.; Arai, T. *J. Photochem. Photobiol. A.* **2004**, *162*, 473.

(12) (a) Yang, G.; Dreger, Z. A.; Li, Y.; Drickamer, H. G. *J. Phys. Chem. A* **1997**, *101*, 7948. (b) Yushchenko, D. A.; Shvadchak, V. V.; Klymchenko, A. S.; Duportail, G.; Pivovarenko, V. G.; Mély, Y. *J. Phys. Chem. A* **2007**, *111*, 10435.

(13) Li, S. Y.; Wang, Q.; Qian, Y.; Wang, S. Q.; Li, Y.; Yang, G. Q. *J. Phys. Chem. A* **2007**, *111*, 11793.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision A.1; Gaussian, Inc., Pittsburgh, PA, 2003.

(15) (a) Deglmann, P.; Furche, F.; Ahlrichs, R. *Chem. Phys. Lett.* **2002**, *362*, 511. (b) Deglmann, P.; Furche, F. *J. Chem. Phys.* **2002**, *117*, 9535.

(16) Andreoni, W.; Curioni, A. *Parallel Comput.* **2000**, *26*, 819.

(17) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.

(18) Brenlla, A.; Rodríguez-Prieto, F.; Mosquera, M.; Ríos, M. A.; Rodríguez, M. C. R. *J. Phys. Chem. A* **2009**, *113*, 56.

(19) (a) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1. (b) Bayliss, N. S.; McRae, E. G. *J. Phys. Chem.* **1954**, *58*, 1002.

(20) (a) Ding, K.; Courtney, S. J.; Strandjord, A. J.; Flom, S.; Friedrich, D.; Barbara, P. F. *J. Phys. Chem.* **1983**, *87*, 1184. (b) Barbara, P. F.; Brus, L. E.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1980**, *102*, 5631. (c) Yin, S. W.; Peng, Q.; Shuai, Z. G.; Fang, W. H. Y.; Wang, Y. H.; Luo, Y. *Phys. Rev. B* **2006**, *73*, 205409.

(21) Guha, D.; Mandal, A.; Koll, A.; Filarowski, A.; Mukherjee, S. *Spectrochim. Acta, Part A* **2000**, *56*, 2669.

(22) (a) Purkayastha, P.; Chattopadhyay, N. *Phys. Chem. Chem. Phys.* **2000**, *2*, 203. (b) LeGourriérec, D.; Kharlanov, V. A.; Brown, R. G.; Rettig, W. *J. Photochem. Photobiol. A* **2000**, *130*, 101.

(23) Kownachi, K.; Kaczmarek, Ł.; Grabowska, A. *Chem. Phys. Lett.* **1993**, *210*, 373.

(24) Takeda, S.; Chihara, H.; Inabe, T.; Mitani, T.; Maruyama, Y. *Chem. Phys. Lett.* **1992**, *189*, 13.

(25) Campbell, I. H.; Smith, D. L.; Tretiak, S.; Martin, R. L.; Neef, C. J.; Ferraris, J. P. *Phys. Rev. B* **2002**, *65*, 085210.

(26) (a) Dreuw, A.; Weisman, J. L.; Head-Gordon, M. *J. Chem. Phys.* **2003**, *119*, 2943. (b) Maitra, N. T. *J. Chem. Phys.* **2005**, *122*, 234104. (c) Magyar, R. J.; Tretiak, S. *J. Chem. Theory Comput.* **2007**, *3*, 976.

(27) (a) Rocco, A. M.; Bielschowsky, C. E.; Pereira, R. P. *Polymer* **2003**, *44*, 361. (b) Costela, A.; Florido, F.; Garcia-Moreno, I.; Duchowicz, R.; Amat-Guerri, F.; Figuera, J. M.; Sastre, R. *Appl. Phys. B: Lasers Opt.* **1995**, *60*, 383.

(28) Muta, H.; Ishida, K.; Tamaki, E.; Satoh, M. *Polymer* **2002**, *43*, 103.

JP900688H