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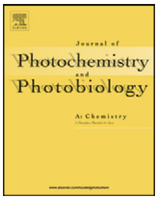

Fluorescence self-quenching and charge transfer of a novel A-σ-π-σ-A type of silicon-bridged compound

Peng Wang, Sheng-Yu Feng*

Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Shanda South Road 27, Jinan 250100, PR China

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ABSTRACT

A novel A-σ-π-σ-A type of silicon-bridged compound, 1,4-bis(cyanophenyldimethylsilyl)benzene (CPDMB), was synthesized and fully characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, HRMS, and single crystal X-ray diffraction. Ultraviolet properties and steady-state fluorescence of CPDMB were studied. The concentration self-quenching phenomena of CPDMB were found in 2-propanol, THF, and CH_2Cl_2. It can be well interpreted by photoinduced self-assembly behavior (J-aggregate) of the CPDMB in solvents. Moreover, the effects of solvents on the fluorescence self-quenching phenomena were also investigated. In order to interpret the novel photoelectric properties of CPDMB, DFT calculations on gas phase CPDMB were carried out.

1. Introduction

Charge transfer is a characteristic feature of organic molecules where electron donor (D) and/or acceptor (A) groups are linked by π-conjugated bridges with *sp*- or *sp*^{2}-carbon structural units such as D-π-A [1,2], D-π-A-π-D or A-π-D-π-A [3–8], D-π-D [9–11] and A-π-A [12] types. Such organic molecules were intensively studied both theoretically and experimentally, due to their novel photoelectric properties, such as nonlinear-optical behavior [8], photon absorption properties [13], solvatochromism [1–12], and so on.

Although the *sp*^{3}-silicon unit is generally a poorer structural motif than *sp*- or *sp*^{2}-carbon groups in facilitating intramolecular electronic communication, conjugated compounds with the silanyl or disilanyl spacers as σ-bridges have been systematically studied. Sakurai and coworkers' investigation on arylsilanes demonstrated that Si–Si bonds and aryl groups function as electron donors and acceptors, respectively [14]. Zyss and co-workers studied the second-order NLO activity of donor–acceptor substituted silanes, which they attributed to the presence of intramolecular CT (ICT) interactions [15,16]. A study by van Walree and coworkers indicated that a single silanyl spacer between two conjugated moieties can facilitate the ICT process [17]. Subsequently, Luh et al. introduced an alternating silanylene spacer as an insulator into alternating co-polymers, which proved that deliberate inclusion of conjugation-interrupting units shows potential to alter and improve the optical and photophysical properties of polymers [18–21]. In addition, diphenylanthracene [22] and anthracene [23] moieties between silanylene spacers have been introduced into molecules to obtain organic light-emitting diodes (OLED) and to study photoinduced energy transfer, respectively.

As classical acceptors, cyanoaryl groups can be used to construct photosensitive compounds [24]. They were also introduced into side-chain of polymers to trace the process of photoinduced polymerization [25]. According to our previous calculations [26], introducing of the cyano substitution to bis(2-thienyl)dimethylsilane can lead to the evident increase of molecular polarity and electrophilicity. In addition, attributed to conformational nonrigidity, manageable properties, and steric effects of the silicon atom, such p-disilanyl-phenyl-bridging compounds as 1,4-bis(dimethyl-4-pyridylsilyl)benzene was prepared and used to construct supramolecular framework with novel channels [27]. However, less photoelectrical studies of p-disilanyl-phenyl-bridging compounds were reported.

In this paper, in order to study the photoinduced charge-transfer mechanisms of p-disilanyl-phenyl-bridging compounds, 1,4-bis(cyanophenyldimethylsilyl)benzene (CPDMB), as a novel A-σ-π-σ-A type of compound, was synthesized and fully characterized. Photoinduced charge-transfer mechanism of CPDMB and corresponding fluorescence self-quenching behavior in solutions were investigated. In order to interpret the novel photoelectric properties of CPDMB, DFT calculations on gas phase were carried out.

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* Corresponding author. Tel.: +86 531 8836 4866; fax: +86 531 8856 4464.
E-mail address: fsy@sdu.edu.cn (S.-Y. Feng).

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2. Experimental

2.1. General procedures and materials

All operations were carried out under dry argon using standard Schlenk techniques. 4-Bromobenzonitrile (Alfa) and other key reagents including n-butyllithium were used as received. The compound 1,4-$ClMe_2SiC_6H_4SiMe_2Cl$ was prepared according to the literature procedures [28]. THF and diethyl ether were distilled from sodium/benzophenone ketyl immediately prior to use in all experiments. The other organic solvents were dried and purified according to standard procedures. Column chromatography was performed on silica gel (200-300 ASTM).

NMR spectra were obtained on a Bruker AC-300/AC-400 NMR spectrometer (^1H, 300.1 MHz or 400.1 MHz; ^{13}C, 75.5 MHz). $CDCl_3$ was used as the solvent for all of the products. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^1H, δ 7.26), internal $CDCl_3$ (^{13}C, δ 76.3). FT-IR spectra were obtained in the 400–4000 cm^{-1} range using a Bruker TENSOR-27 FTIR Spectrometer. Mass spectra were recorded on an Agilent Q-TOF6510 Mass Spectrometer. Solution UV spectra were measured using a HITACHI U-4100 spectrophotometer in spectrophotometric grade solvents. Solid state UV spectra were measured on a Shimadzu UV-2500 spectrophotometer. The steady-state fluorescence spectra were recorded with a PerkinElmer LS 55 spectrofluorimeter. The emission lifetime measurements were carried out on FL920 fluorescence lifetime spectrometer. X-ray crystallography was performed on a Bruker Smart 1000 diffractometer at room temperature (25 °C).

2.2. Synthesis of $CNC6H4Me_2SiC_6H_4SiMe_2C_6H_4CN$ (CPDMB)

To n-BuLi (5mmol) in hexanes/diethyl ether (2/10 mL) mixed solvents, a solution of 4-bromobenzonitrile (0.91 g, 5 mmol) in THF (10 mL) was added at −78 °C [29]. After addition, the mixture was kept at −78 °C for 30 min, and then a solution of 4-$ClMe_2SiC_6H_4SiMe_2Cl$ (0.60 g, 2.5 mmol) in THF (10 mL) was added dropwise. After 2 h, the mixture was warmed to room temperature and then quenched by appropriate amount of water. The volatiles were removed from the resulting mixture by vacuum distillation. The residue was purified by column chromatography using dichloromethane/n-hexane following by ethyl acetate as eluent to afford 0.80 g of $CNC_6H_4Me_2SiC_6H_4SiMe_2C_6H_4CN$ as a white solid (80.8%). IR (cm^{-1}) (KBr): 2224 (CN), 1252, 823, 788 (Si–Me), 1099 (Si–Ar), 1824, 1929 (central Ar); ^1H NMR, δ 0.59(s, 12H, MeSi), 7.50(d, 8H, Ph–H/Si-β-H), 7.63(d, 4H, Ph–H/Si-γ-H); ^{13}C NMR, δ −2.85(MeSi), 118.91 (CN), 112.81, 131.07, 133.59, 134.59, 138.16, 144.96 (Ph–C); MS (*m/z*): 397.15 $[M+H]^+$, 397.15 (Anal. Calcd.).

2.3. Synthesis of $CNC_6H_4SiMe_2C_6H_4CN$ (DCPDM)

The colorless crystal of di(4-cyanophenyl)dimethylsilane (DCPDM) was prepared by the reaction of n-BuLi, 4-bromobenzonitrile and dimethyldichlorosilane in accordance with the same procedures by using Me_2SiCl_2 instead of 4-$ClMe_2SiC_6H_4SiMe_2Cl$. The yield was 35.5%. IR (cm^{-1}) (KBr): 2223 (CN), 1255, 850–780 (Si–Me), 1100 (Si–Ar); ^1H NMR, δ 0.63 (s, 6H, MeSi), 7.59–7.61 (d, 4H, Ph–H), 7.65–7.67 (d, 4H, Ph–H); ^{13}C NMR, δ −3.05 (MeSi), 118.63 (CN), 113.37, 131.28, 134.53, 143.45 (Ph–C).

2.4. Quantum chemistry calculations

To gain insight into the electric and optical properties of CPDMB, DFT calculations in gas phase were performed using the Gaussian 03 program package [30]. Hybrid B3LYP exchange-correlation functional [31] and 6-31+G basis set [32] were employed in consideration of both accuracy and efficiency. The ground-state geometry of CPDMB was optimized in gas phase by a standard force-minimization procedure.

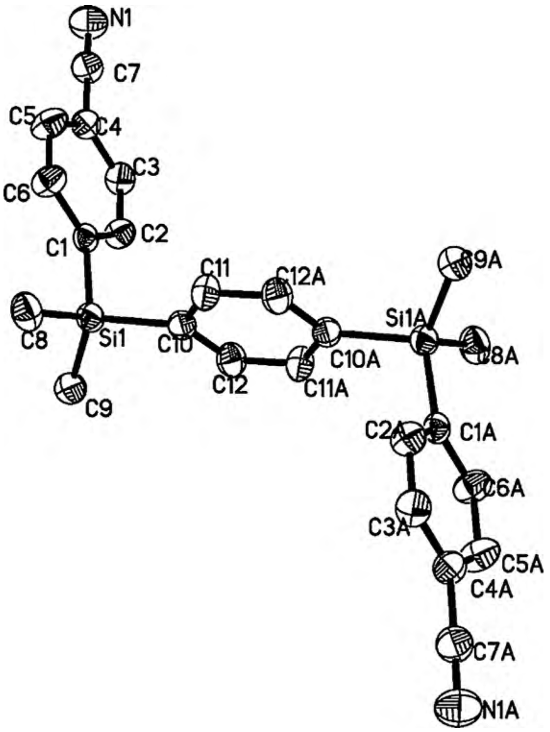


Fig. 1. Molecular structure of CPDMB and selected bond distances (Å) and angles (deg): Si1–C1 1.884(3), Si1–C8 1.867(3), Si1–C10 1.893(3), C7–N1 1.150(3); C9–Si1–C8 112.0(2), C9–Si1–C1 108.03(15), C9–Si1–C10 110.68(15), C6–C1–C2 115.9(2), C3–C2–C1 123.1(3), and N1–C7–C4 178.2(3).

3. Results and discussion

3.1. Synthesis

Limited by rigorous temperatures for lithiation of halogenated benzonitriles [33], cyanophenyl silanes were prepared generally through reaction of bromophenylsilane and copper(I) cyanide [17]. The latest paper [29] reported that mixed solvents (THF/diethyl ether) and reverse addition from bromobenzonitriles to n-BuLi can increase the yield of lithiated benzonitriles. According to such optimized method, we prepared the target molecule CPDMB with p-disilanyl-phenyl-bridge in higher yield (80.8%) by the reactions of 4-lithiobenzonitrile with 4-$ClMe_2SiC_6H_4SiMe_2Cl$. The experiments show that the method used in this work provides competitive yield of cyanophenyl silanes without heavy metallic salt. Similarly, the reference compound DCPDM was also obtained successfully according to this procedure.

3.2. Molecular structure of CPDMB

The molecular structure of CPDMB has been determined by single-crystal X-ray diffraction (Fig. 1 and Table 1). It crystallizes in space group (*P21*/*n*). The single molecule has a crystallographically imposed centre of inversion, and two molecules fill the monoclinic unit cell.

In the crystalline state of CPDMB, the planes of benzene rings in the two cyanophenyl moieties are parallel to each other. The plane of benzene ring in p-disilanyl-phenyl-bridging unit is nearly perpendicular (79.5°) to these two planes although the angles around silicon atoms (there into C9–Si1–C1, 108.03°; C1–Si1–C10, 107.26°; C8–Si1–C1, 109.16°; C8–Si1–C10, 109.56°) follow the

Table 1
Crystallographic data for CPDMB.

	CPDMB
Empirical formula	$C_{24}H_{24}N_2Si_2$
Fw	396.63
Cryst syst	Monoclinic
Space group	*P21/n*
a, Å	12.721(10)
b, Å	6.154(5)
c, Å	15.109(11)
α, deg	90.00
β, deg	103.610(13)
γ, deg	90.00
V, Å^3	1149.6(15)
Z	2
Dc, g cm^{-3}	1.14576
No. of rflns collected	5092
No. of unique data	1869
R_{int}	0.0413
$\theta_{\max}$, deg	24.31
R_1 ($I > 2\sigma(I)$)	0.0477
wR_2 (all data)	0.0691

rules of tetrahedron character. Moreover, the angles C6–C1–C2 (115.9°) and C11–C10–C12 (115.2°) are smaller, while the angles C5–C6–C1 (122.3°), C3–C2–C1 (123.1°), C10–C11–C12A (122.2°), and C10–C12–C11A (122.3°) are bigger indicating that the configurations of benzene rings were influenced by the σ–π interaction of silicon-spacer and benzene rings. The slightly bent cyano group (N1–C7–C4 = 178.2°) is nearly on the plane of the benzene ring in cyanophenyl moiety which can provide the excellent conjunction for the intramolecular charge-transfer (IACT).

3.3. Electronic absorption spectra

Electronic absorption spectra of CPDMB in 2-propanol, THF, CH_2Cl_2, and solid state are shown in Fig. 2. Maximum absorption wavelength and corresponding molar extinction coefficients of CPDMB and reference compound DCPDM are compiled in Table 2. No additional band was found in absorption spectra of CPDMB compare to those of DCPDM. Whereas, compared with the DCPDM in 2-propanol, the higher molar extinction coefficients of CPDMB were found. Two bands at 237 nm and 271 nm (in 2-propanol), 274 nm (in THF), and 277 nm (in CH_2Cl_2) (Fig. 2) can be referred to ^1L_a and ^1L_b bands of CPDMB, which were labeled by Platt [34] for different transitions from the ground states to different excited singlet electronic states of aromatic system. The same as discussion of di(4-cyanophenyl)dimethylsilane (DCPDM) [17], the shorter wavelength bands named ^1L_a are predominantly based on the promotion of an electron from the highest-occupied molecular orbital (HOMO) to the second-lowest-unoccupied molecular orbital (SLUMO) named S_2 mechanism. The longer wavelength bands named ^1L_b correspond to a HOMO–LUMO transition (S_1 mechanism). Compared with analogous systems such as 1,1′-bicyclohexyliden-4-ylidenepropanedinitrile [35], the 237 nm can also be assigned to $\pi \rightarrow \pi^*$ transition of cyano acceptor, and the weaker band at 271/274/277 nm can be ascribed to a transition involving charge transfer from the benzene ring to cyano acceptor. In absorption spectra of different concentrations of CPDMB in the three solvents, no obvious change of band shape was found. Besides, no obvious σ-to-π charge-transfer absorptions over 300 nm were found in the spectra, indicating that the p-disilanyl-phenyl-bridge in CPDMB does not serve as conductor but insulator for chromophores in ground state. The through-bond interaction of the two cyanophenyl groups was forbidden in ground state.

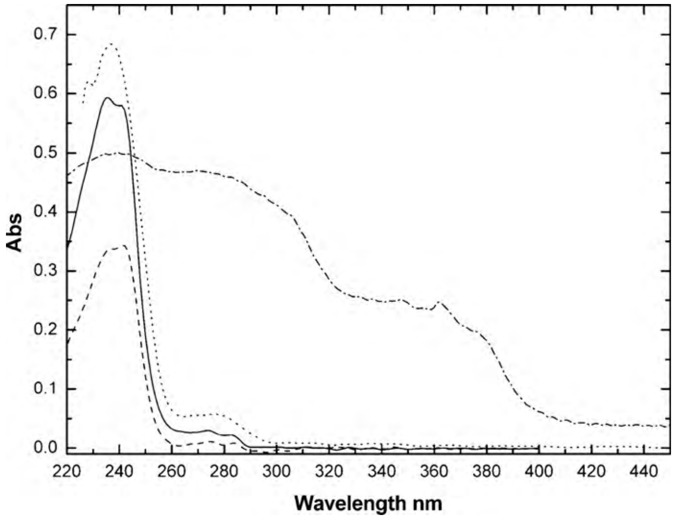


Fig. 2. Solution (9.0×10^{-5} M) absorption spectra of CPDMB in 2-propanol "—", THF "—", CH_2Cl_2 "...", and the solid state absorption spectrum of CPDMB "- -".

3.4. Ground state excitation and emission fluorescence

The ground state excitation spectra and photoluminescence spectra of CPDMB were characterized in 7 different solvents, n-Bu_2O, 2-propanol, THF, chloroform, methanol, DMSO, and CH_2Cl_2 (Fig. 8 in SI). The shifts of excitation bands of CPDMB in different solvents are more obviously than emission ones. Obviously, there are no solvent effects on the fluorescence bands to be observed at 307 nm in 6 different solvents except DMSO (Fig. 8(B) in SI). In contrast, the red shift of the broad fluorescence band at longer wavelength in DMSO was observed, indicating that the emitting state are polar, which can be treated as the orthaonol intramolecular charge transfer (OICT) state occurring by stabilizing the CT states in polar solvents, as reported on aryldisilanes [36]. Whereas, the stocks shifts of CPDMB are not solvent-polarity dependent, which means weak IACT in CPDMB molecule even in excited state.

3.5. Self-quenching behavior

The concentration dependent excitation and emission spectra of CPDMB were found in THF and 2-propanol (see Fig. 3). As shown in Fig. 2(A) and (C), the excitation bands at 237 nm lower and excitation bands at 274/271 nm grow with concentration of CPDMB from 1.0×10^{-5} to 4.0×10^{-4} mol L^{-1}. Also, the original excitation bands at 237 nm were red shifted following the increase of concentration in certain range.

For intensive study of the influences from the excitation spectra of solvents, the excitation spectra of CPDMB in solid state, THF, and 2-propanol were characterized, separately. Two excited bands at 218 and 248 nm of CPDMB in solid state were found (Fig. 9(A) in SI). It means that there are nearly 30 nm red-shifts of excited bands of CPDMB in both solvents. Also some shoulders of excitation band were found at longer wavelength, which means the aggregation of monomer in solid state. To study the interaction of solvents and solute, the excitation bands of 2-propanol and THF were found at 250 and 257 nm, separately (Fig. 9(B) in SI), which can be attributed to n–σ* electron transitions of O atoms with lone-pair electrons in molecular structures [37]. There are three major interactions between cyanophenyl group and solvent molecule: (1) dipole–dipole interaction, (2) a hydrogen-bond-like interaction that the protic solvent partially donates hydrogen atom to the π-cloud of the nitrile triple bond, and (3) a second hydrogen-bonding interaction between one of the ring-hydrogen atoms and the lone pair electrons of the O or N atom in the solvent molecule [38,39]. However, the same phenomenon was also found in CH_2Cl_2 (Fig. 10 in SI), which indicates that neither (2) nor (3) is the defini-

Table 2
The λ_{max} (nm) and extinction coefficient (β, 10^{-3} mol^{-1} L cm^{-1}) of CPDMB and DCPDM.

Compounds	CPDMB		DCPDM	
	λ_1 (ε_1)	λ_2 (ε_2)	λ_1 (ε_1)	λ_2 (ε_2)
THF	237 (37.6)	274 (2.29)	–	–
2-Propanol	237 (64.8)	271 (4.03)	237 (26.3)	279 (1.52)
CH_2Cl_2	237 (76.0)	277 (6.39)	–	–

tive factor for concentration dependent excitation of the CPDMB.

The corresponding emission spectra of CPDMB in 2-propanol (Fig. 2(B)), THF (Fig. 2(D)), and CH_2Cl_2 (Fig. 10(B, C) in SI) were also shown. Clearly, the fluorescence excited at 237 nm was quenching, and fluorescence excited at 274/271 nm was strengthened with the increase of concentration. The linearly concentration dependence of the fluorescence intensities in 2-propanol, THF, and CH_2Cl_2 are shown in Fig. 4(A). Obviously, the Stern–Volmer plots of quenching fluorescence (Fig. 4(B)) cannot be fitted to linear, which means that the fluorescence excited at 237 nm is quenched by not only monomer, but also aggregator. The enhanced fluorescence intensity excited at longer wavelengths shows that the quenching energy is mainly released by radiation, indicating that the quenching was not caused through collision but through charge-transfer or energy-transfer mechanism between molecules. Moreover, the emission lifetimes of CPDMB in 2-propanol at different concentrations (1×10^{-6}, 1×10^{-4}) were measured (Fig. 11 in SI). Both excited wavelengths at 237 and 271 nm at two concentrations were used to measure the emission lifetimes. Although the emission lifetime excited at 271 nm cannot be got for weak emissions, the other three lifetimes were measured to be 6.65 ns (1×10^{-6}, 237 nm), 6.58 ns (1×10^{-4}, 237 nm), and 6.51 ns (1×10^{-6}, 271 nm). Consequently, the decrease of lifetime was not obviously (~0.1 ns) following the aggregation behavior, which can be interpreted by concomitant monomer species at high concentrations.

Generally, donor–acceptor systems with cyanophenyl as an acceptor group always show novel and classic photoelectric properties such as IACT [40]. However, according to solvent-polar

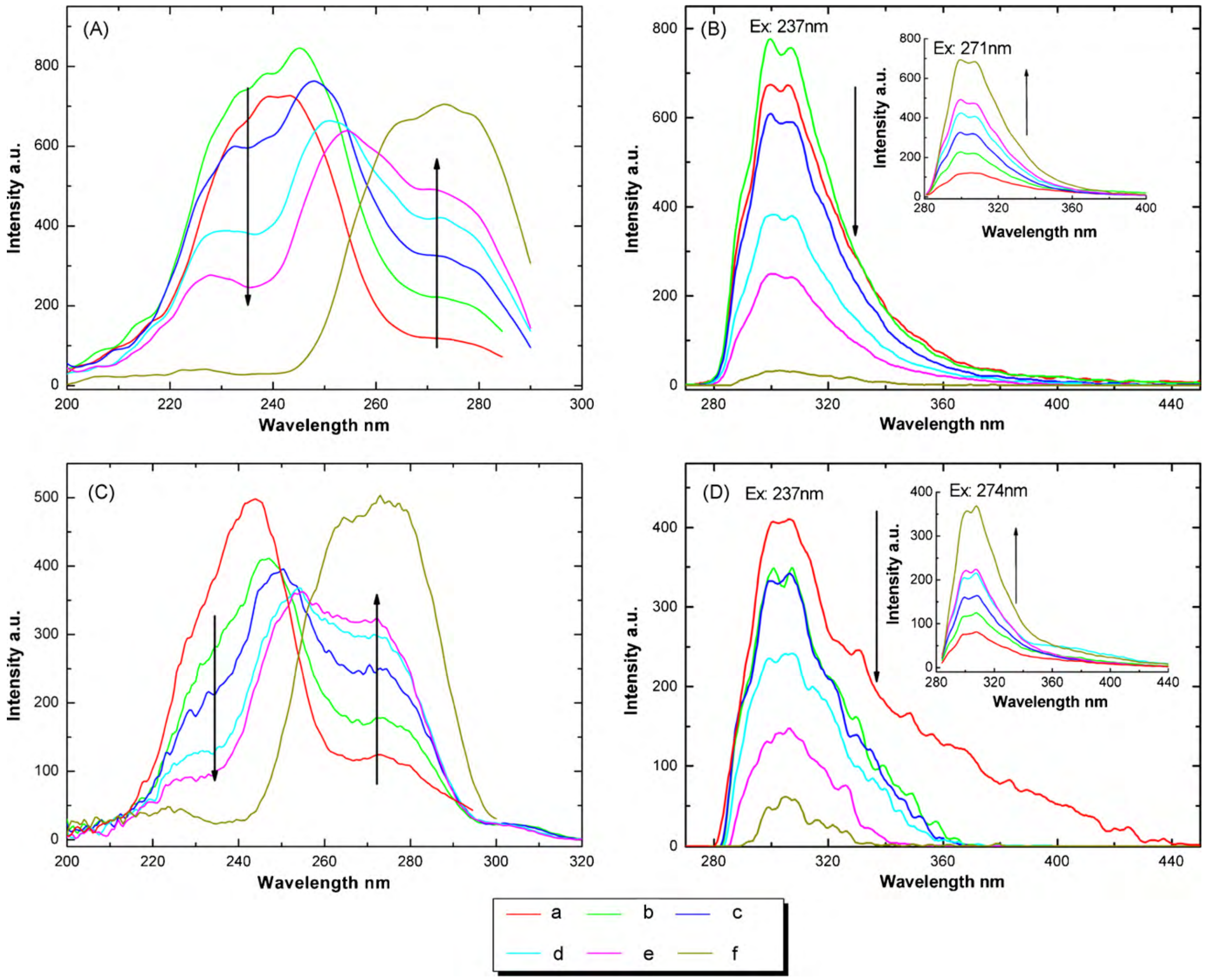


Fig. 3. Excitation and fluorescence spectra of CPDMB in solutions at room temperature with the concentration at (a) 1.0×10^{-5} M, (b) 3.0×10^{-5} M, (c) 5.0×10^{-5} M, (d) 7.0×10^{-5} M, (e) 9.0×10^{-5} M, and (f) 4.0×10^{-4} M. 2-propanol: (A) Excitation spectra with the emission at 300 nm. (B) Fluorescence spectra excited at 237 nm and 271 nm. THF: (C) Excitation spectra with the emission at 300 nm. (D) Fluorescence spectra excited at 237 nm and 274 nm.

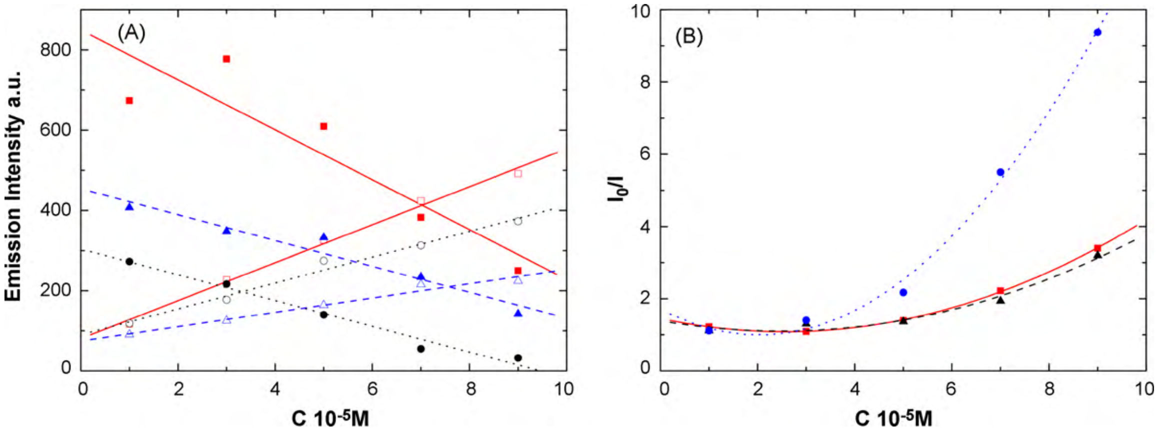


Fig. 4. (A) Fluorescence intensities (λ_{em} = 300 nm) of CPDMB in 2-propanol (red), THF (black), CH_2Cl_2 (blue) at different concentrations: solid points (λ_{ex} = 237 nm) and hollow points (λ_{ex} = 271/274/274 nm); (B) Stern–Volmer plots of CPDMB self-quenched in 2-propanol (red), THF (black), CH_2Cl_2 (blue) (λ_{ex} = 237 nm, λ_{em} = 300 nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

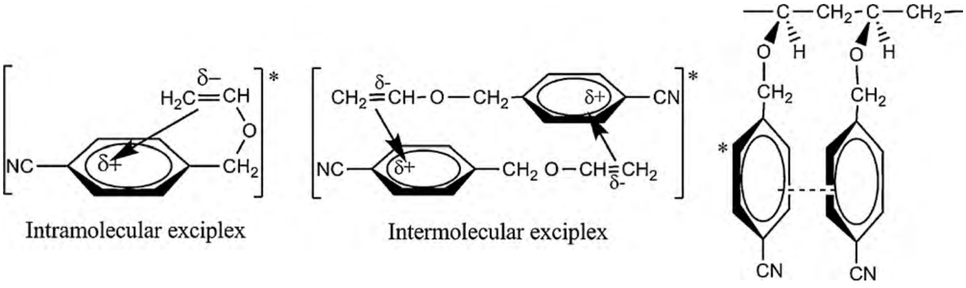
independent stead-state fluorescence properties of the CPDMB, the through-bond interaction of the two cyanophenyl moieties is weak. It indicates that the IACT between two cyanophenyl groups in CPDMB molecule is forbidden by p-disilanyl-phenyl-bridge. So the charge transfer or energy transfer of the CPDMB molecules occur through-space instead of through-bond. As reported by Li et al. [25], fluorescence "structural self-quenching effect" (SSQE) can be observed for polymers with vinyloxy monomer bearing cyanophenyl moiety. The SSQE was considered to be ascribed to the formation of a charge transfer exciplex between the electron-accepting chromophore and the coexisting electron-donating carbon–carbon double bond upon UV light irradiation. For interpreting SSQE, the formations of exciplex between the cyanophenyl and the vinyloxy group upon UV irradiation as well as mutual interaction between adjacent cyanophenyl were described in Scheme 1. In our systems, due to the steric hindrance effects in molecule and structural properties of silicon atoms, two cyanophenyl groups cannot locate at the same side of central-phenyl-ring-plane but locate at both sides of central-phenyl-ring-plane, and they even parallel each other as shown in crystal structure (Fig. 1). So through-space intramolecule interaction of the two cyanophenyl moieties was forbidden. Therefore, formation of intermolecular exciplex between CPDMB molecules is most possible. In addition, crystal structure stacking can be treated as structure of aggregates ($N=\infty$). Also, compared with H-aggregates, J-aggregates in particular are very seldom observed because only a few molecules form J-aggregates have been clearly identified [41]. And concentration-dependent excitation of CPDMB in solvents at certain concentration range (1.0×10^{-5}–9.0×10^{-5} M) proved the aggregation of the CPDMB. As shown in Fig. 3(A) and (C), the excitation band at shorter wavelength was gradually red shifted with the increase of concentration, and the excitation band at longer wavelength gradually grew at the same time. So it can be attributed to J-aggregation according to Kasha's exciton theory [42]. The relation of band shifts with concentration follows:

$$\Delta\nu=\frac{2(N-1)\mu^2}{hcNr^3}(1-3\ \cos^2\alpha) \qquad (1)$$

where the $\Delta\nu$ is the separation between wavenumbers of aggregate and monomer, h is Planck constant, c is the velocity of light, μ is transition (dipole) moment, r is the distance between two dipoles, α is the angle made by the polarization axes of the unit molecule with the line of molecular centers. When $\alpha<54.7^\circ$, the molecule will be J-aggregate; when $\alpha>54.7^\circ$, the molecule will be H-aggregate. Although some parameters in equation cannot be obtained easily, the type of aggregation can be confirmed by value of α angle. In the crystal packing structures of CPDMB, acceptor sites on neighboring molecules are oriented parallel to each other. To obtained the value of α angle, the center-to-center distance of benzene rings (r_{cc}) among CP of neighboring molecules was confirmed to be 4.846 Å, and the distances of two CP-planes (r_{pp}) was confirmed to be 3.562 Å. So α angle can be confirmed to be 47.3° according to Eq. (2):

$$\sin\ \alpha=\frac{r_{pp}}{r_{cc}} \qquad (2)$$

So the concentration self-quenching behavior of CPDMB can be attributed to J-aggregation of the molecules in higher concentrations (>10^{-5} mol L^{-1}), which can be represented in the model and corresponding crystal structure stacking picture (Fig. 5). In addition, gradual growth of the excitation band at longer wavelength can be attributed to intermolecular charge transfer (IECT) from the benzene ring of cyanophenyl to the cyano acceptor of neighboring molecule.



Scheme 1. Exciplex model of SSQE [15].

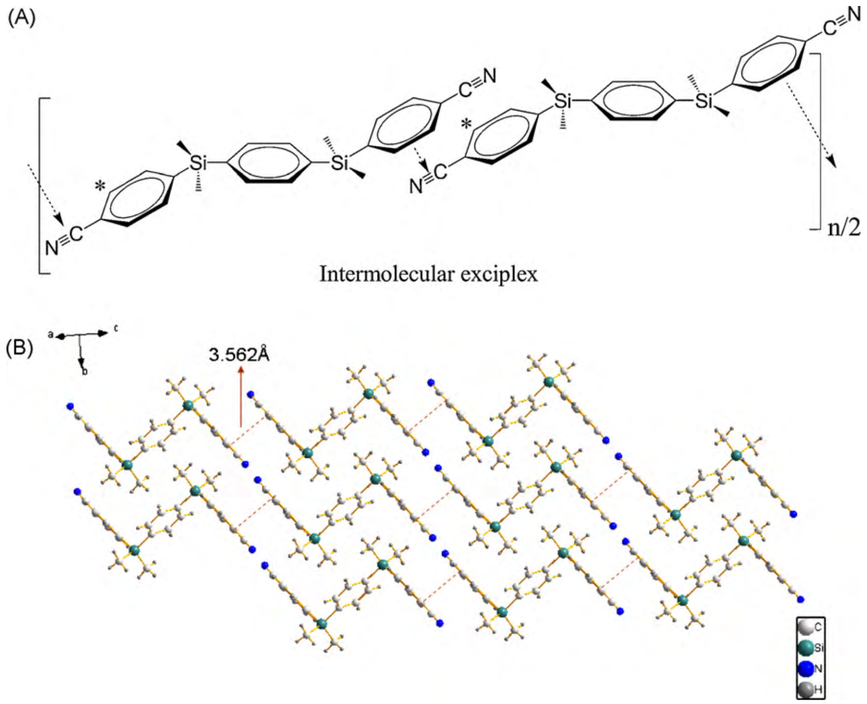
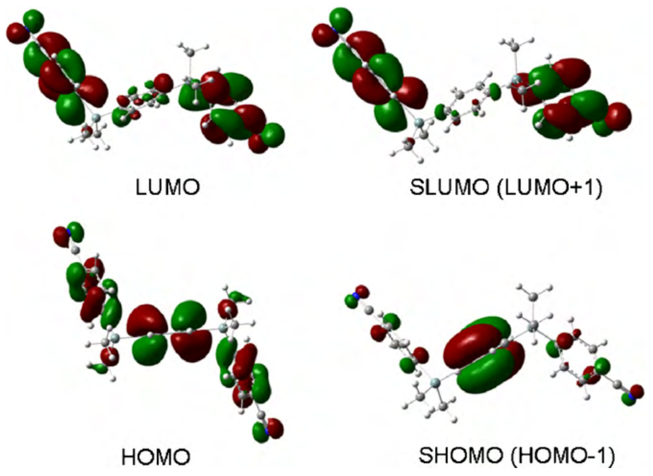


Fig. 5. Exciplex model of J-aggregate of CPDMB (A) and corresponding crystal structure stacking picture (B).


LUMO

SLUMO (LUMO+1)

HOMO

SHOMO (HOMO-1)

Fig. 6. Frontier orbitals calculated for CPDMB in the gas phase at the DFT level (isodensity = 0.02 au).

3.6. Theoretical calculations

In order to interpret the novel photoelectric properties of CPDMB, DFT calculations were carried out. The frontier orbitals contributing to the electronic transition were sketched in Fig. 6, the HOMO mainly locates on the benzene ring of p-disilanyl-phenyl-bridge and partly on the cyanophenyl groups (acceptor), and LUMO shows a significant density on the cyanophenyl groups of CPDMB and some on the benzene ring of p-disilanyl-phenyl-bridge. Moreover, there is less density of delocalized electrons on the benzene ring of p-disilanyl-phenyl-bridge at the SLUMO level. It means that during the two excitation processes (HOMO → LUMO and HOMO → SLUMO), the benzene ring of p-disilanyl-phenyl-bridge and the two cyanophenyl groups act as the electron-donor and electron-acceptors, respectively. During the both processes, the electrons were almost localized in both cyanophenyl groups, and delocalization can hardly spread the whole molecule, which was also reported for DCPDM [17]. Whereas, these processes increase the density of the electron around cyanophenyl groups, which help to enhance the IECT between adjacent cyanophenyl groups. So the concentration self-quenching fluorescence of CPDMB can be well interpreted by enhanced IECT between J-type aggregated CPDMB molecules.

4. Conclusions

An A-σ-π-σ-A type of silicon-bridged compound, 1,4-bis(cyanophenyldimethylsilyl)benzene (CPDMB), was synthesized and characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, HR-MS, and single-crystal X-ray diffraction. The novel concentration self-quenching phenomena in different solvents at higher concentrations ($>10^{-5}$ mol L^{-1}) were found. The phenomena can be well interpreted by the photoinduced self-assembly (J-aggregation) of CPDMB in solvent, which was also shown in crystal structure stacking picture. According to solvent-independent stocks shifts and frontier bonds analysis, IACT between two cyanophenyl groups in CPDMB is nearly forbidden. Moreover, donor ability and structural effects of p-disilanyl-phenyl-bridge in molecule enhance the IECT of CPDMB. IECT of CPDMB in solvents open up for a new charge-transfer type of silicon-bridged compounds.

Supplementary material

FT-IR spectra, ^{1}H NMR spectra, ^{13}C NMR spectra of CPDMB and DCPDM; HRMS spectra, Crystallographic Data, and fluorescence spectra (in CH_2Cl_2) of CPDMB were given. Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-758060 for CPDMB, and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. [Fax: Internet C44 1223/336 033 E-mail: deposit@ccdccam.ac.uk].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.07.002.

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