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RESEARCH ARTICLE

A novel NIR violanthrone derivative with high electron-deficiency: effect of fluorescence on dicyanomethylene substitution

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Near infrared (NIR) dyes attracted increasing interests in widely potential applications, such as fluorescent probe and living organism imaging, due to their low background signals from biomolecules, low light scattering and deep penetration, and low-cost excitation light sources. A novel NIR violanthrone derivative (VA-CN) with dicyanomethylene substitution was synthesized and fully characterized by ^{1}H NMR, ^{13}C NMR, HRMS, and IR spectrometry. It is demonstrated that the original planar conformation of violanthrone ring (the nine fused benzene rings) becomes twisted and unsymmetrical upon the incorporation of two strong electron-withdrawing dicyanomethylene units. Photophysical, electrochemical performances as well as distinct solvatochromic effects were studied in detail. Considering the low reduction potential (-0.56 V vs NHE), VA-CN could be considered as a good electron acceptor due to the strong electron deficiency resulted from dicyanomethylene group. A distinct increase in fluorescence was observed with 30-fold enhancement upon the addition of *n*-butyl amine. The reversible fluorescence "*off-on*" shows that VA-CN might be served as a promising fluorescent sensor for electron-rich amines.

Keywords violanthrone derivative, dicyanomethylene group, synthesis, NIR fluorescence

1 Introduction

Near infrared region (NIR) dyes have become an increasingly interesting field in widely potential applications, such as fluorescent probe and living organism imaging, due to their low background signals from biomolecules, low light scattering and deep penetration, and low-cost excitation light sources [1–3]. Among NIR dyes, cyanine, squarylium, and boron-dipyrromethene (BODIPY) dyes have been deeply developed [4–12]. Meguellati et al. has reported an NIR family of unsymmetrical imine-based trimethine and pentamethine cyanine dye analogs that could form under reversible and thermodynamically controlled conditions from building blocks of non- or weakly emissive amine and aldehyde [4]. More recently, Umezawa et al. has successfully studied a series of bright and color-tunable fluorescent dyes over a wide range including NIR by introducing electron donors and acceptors to BODIPY segment [1]. However, there is still much room to develop various types of NIR dyes with high molar extinction coefficients, longer emission wavelength, and sharp and intense fluorescence with high chemical and photo stabilities.

Violanthrone, a system fused with nine benzene rings, is a well-known traditional anthraquinone vat dyestuff for cotton coloration with high light fastness, high washing, and chlorine bleaching. 16,17-dialkoxy violanthrone have been applied in the area of NIR military and anti-counterfeiting techniques because of its highly conjugated system. Recently, several groups are engaged in its photochemical properties and conductivity [13–16]. However, as an NIR fluorescent dye, the emission peak of 16,17-dialkoxy violanthrone is located at near 710 nm and not far from the visible red light region (almost 40% ratio in the range of 650 – 700 nm), thus bringing a very serious disturbance from the visible light region. With this in mind, in this article we report a new type of NIR fluorescent dye (VA-CN, Figure 1) based on violanthrone via the incorporation of strong electron-withdrawing dicyanomethylene unit. Interestingly, the original planar conformation of violanthrone ring (the nine fused benzene rings) becomes twisted and unsymmetrical upon the incorporation of two strong electron-withdrawing dicyanomethylene units. Its fluorescent efficiency on dicyanomethylene substitution was also discussed in detail.

2 Experimental

Violanthrone was commercially purchased and washed with methanol. Tetrabutylammonium hexafluorophosphoric was purchased from Aldrich. All other chemicals and solvents were obtained from Sinopharm Chemical Reagent Co., Ltd,

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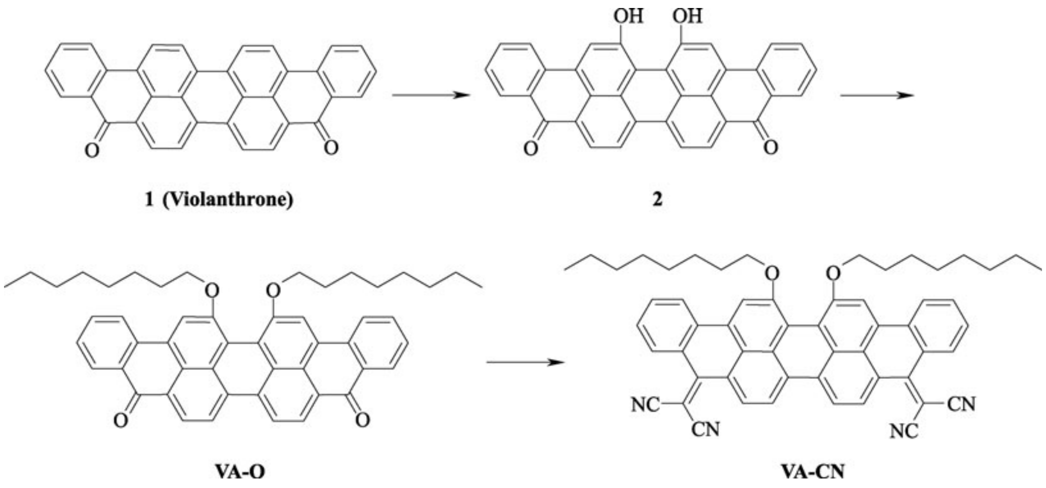


Figure 1 Synthetic route of NIR fluorescence dyes VA-O and VA-CN.

China (reagent grade) and used as received. The synthesis of 16,17-dihydroxy violanthrone (2) was performed according to Ref. [17].

^{1}H NMR and ^{13}C NMR spectra were obtained by using a Brucker AM-400 spectrometer. The mass spectra were conducted on a HP5989 mass spectrometer. UV-Vis spectra were recorded on a Varian Cary 500 spectrophotometer, and fluorescence spectra on a Varian Cary Eclipse fluorescence spectrophotometer. Cyclic voltammogram was determined with Versastat II electrochemical workstation (Princeton Applied Research) using a platinum electrode as working electrode, a platinum wire as counter electrode, and a Ag/AgCl electrode in saturated KCl solution as reference electrode. Tetrabutylammonium hexafluorophosphoric ($0.1\ \mathrm{mol\cdot L^{-1}}$) was used as supporting electrolyte, and ferrocene was used as internal reference.

The geometrical, electronic, and optical properties of VA-O and VA-CN were calculated using Gaussian 03 program package [18]. The molecular structures were optimized using hybrid B3LYP exchange-correlation functional and the all-electron 6–31 g (d) double-ξ plus polarization basis set [19]. For the excited state calculation, we employed the 6–31 + g (d) double-ξ plus polarization and diffuse basis set. The ground-state geometries have been optimized in both vacuum and solution by a standard force-minimization procedure. Solvation effects were evaluated by means of polarizable continuum model [20].

2.1 Synthesis of 16,17-dioctyloxyviolanthrone (VA-O)

To a mixture of 16,17-dihydroxyviolanthrone (5.0 g, 0.01 mol) and potassium carbonate (10.3 g, 0.075 mol) in DMF (35 mL) heated to 120°C, 1-bromooctane (13.9 g, 0.05 mol) was added during 3 h. The reactant was heated to about 130°C and stirred for another 8 h and then cooled and poured into water (100 mL). The solid was filtered and recrystallized with methanol and ethyl acetate, respectively. Compound VA-O was acquired as black solid (yield 12.5%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.41 (d, J = 6.8 Hz, 2H), 8.39 (d, J = 1.2 Hz, 2H), 8.28 (d, J = 8.0 Hz, 2H), 8.18 (d, J = 8.0 Hz, 2H), 8.10 (s, 2H), 7.76 (t, J = 7.2 Hz, 2H), 7.54 (t, J = 7.6 Hz, 2H), 4.19 (t, 4H), 1.85 (m, 4H), 1.45 (m, 4H), 1.30 (m, 16H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 182.4, 155.5, 135.2, 133.5, 132.8, 130.6, 128.5, 128.3, 127.9, 127.0, 126.8, 126.4, 122.8, 122.0, 116.5, 112.5, 69.1, 31.8, 29.8, 29.6, 29.3, 26.0, 22.7, 14.1. IR, ν ($\mathrm{cm^{-1}}$): 2925, 2851, 1740, 1380, 750.

2.2 Synthesis of VA-CN

Compound VA-O (5.0 g, 4.9 mmol) and dicyanomethylene (1.5 g, 22.7 mmol) were added into acetic anhydride (30 mL). The mixture was stirred and refluxed for 6 h, then cooled and poured into hot water (100 mL). The solid was filtered and washed with ethanol (200 mL). After recrystallized with ethyl acetate, the dark green product was further purified by column chromatography on silica using CH_2Cl_2/petroleum ether 4:1 (v/v) as elute. VA-CN was obtained as green solid (yield 11.3%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.60 (d, J = 7.6 Hz, 2H), 8.48 (d, J = 7.6 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 8.4 Hz, 2H), 8.32 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.23 (s, 1H), 8.18 (s, 1H), 7.84 (t, J = 7.2 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 4.31 (t, 4H), 1.95–1.87 (m, 4H), 1.45 (t, J = 7.2 Hz, 4H), 1.29 (m, 16H), 0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 182.7, 182.5, 160.1, 156.3, 156.0, 135.3, 135.0, 133.9, 133.1, 132.9, 132.8, 132.5, 130.7, 130.5, 129.0, 128.5, 128.2, 128.0, 127.9, 127.6, 127.5, 127.3, 127.2, 126.6, 125.5, 124.0, 123.3, 123.1, 122.9, 122.8, 122.3, 121.4, 120.3, 117.0, 116.8, 116.5, 116.2, 113.1, 112.6, 112.2, 69.5, 31.8, 29.9, 29.5, 29.3, 26.2, 22.6, 14.1. IR, ν (cm^{-1}): 2925, 2851, 2210, 1380, 750. FAB-MS: calc. for [$C_{56}H_{48}O_2N_2 + Na^+$]: 831.3675, found: 831.3660.

3 Results and discussion

3.1 Synthesis

Violanthrone, used as starting material, shows poor solubility in most organic solvents due to its relatively strong rigidity and polarity. While long alkoxy substituents on the bay of violanthrone were introduced, its solubility can be improved significantly [17]. Therefore, compound violanthrone was oxidized into 16,17-dihydroxy violanthrone and two long tail n-octyloxy groups were then incorporated through Williamson reaction (Figure 1). The resulted compound VA-O can be dissolved in common organic solvents, such as CH_2Cl_2, toluene, CCl_4, ethyl acetate (EA), THF, and DMF.

Meanwhile, it is necessary to increase the bipolarity between donor and acceptor for the sake of red-shift in the absorption maxima to near infrared area. As is well known, cyano group is a kind of very strong electron-acceptor that is broadly applied in many intramolecular charge-transferring (ICT) systems [21–23]. Therefore, four cyano groups (two strong electron-withdrawing dicyanomethylene unit) were incorporated into carbonyl groups through Knoevenagel reaction (VA-CN, Figure 1). Notably, since the carbonyl groups in the violanthrone system are much less reactive due to the large conjugation system of violanthrone, the target compound could not be obtained through most traditional Knoevenagel reaction conditions [24]. Finally, we successfully synthesized VA-CN via using acetic anhydride as both solvent and catalyst. Its chemical structure was fully characterized by ^{1}H NMR, ^{13}C NMR, HRMS, and IR spectra.

As a comparison of the ^{1}H NMR spectra between VA-O and VA-CN (Figure 2), there is no obvious difference between the signals of saturated hydrogen atoms ($H_h - H_o$, $H'_h - H'_o$) since the long tail n-octyl group is not near to the π-delocalization system. While the dicyanomethylene unit is introduced into VA-O, the enhancement of electron-withdrawing capability makes the molecular polarity of VA-CN higher in electron distribution, thus resulting in an obvious change in chemical shift for aromatic hydrogens. As expected, the chemical shifts corresponding to $H_a - H_g$ in the parent ring of VA-O are located at 8.41, 8.28, 8.39, 7.54, 7.76, 8.18 and 8.10 ppm, respectively, presenting a relatively good symmetry. However, with respect to VA-O, all signals corresponding to the parent ring hydrogen in VA-CN shift to downfield and are split. The chemical shifts of and $H''_a - H''_g$ in VA-CN were 8.60, 8.48, 8.38, 8.32, 8.23, 7.84, 7.67 ppm (for $H'_a - H'_g$) and 8.60, 8.42, 8.38, 8.28, 8.18, 7.78, 7.55 ppm (for $H''_a - H''_g$), respectively. Moreover, two split peaks with equal integrity in VA-CN are observed. For example, in the compound VA-O, H_g is a sharp single peak, representing two symmetric hydrogen atoms. In VA-CN, two single peaks with equal integrity correspond to H'_g and H''_g, thus indicating that the chemical environment of H'_g is different from H''_g. In the case of VA-CN, the split for such aromatic hydrogens in NMR signals obviously indicates that the original planar conformation of violanthrone ring (the nine fused benzene rings) becomes twisted and unsymmetrical upon the incorporation of two strong electron-withdrawing dicyanomethylene unit.

To gain insight into the twisted conformation, the optimized ground state geometries of VA-O and VA-CN were calculated using Gaussian 03 program. Optimized structures of VA-O and VA-CN are shown in Figure 3, and characteristic

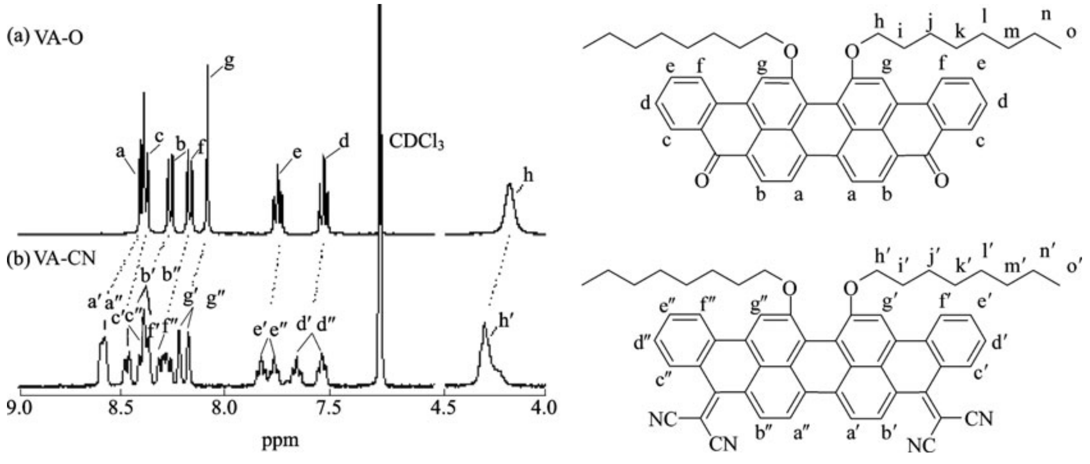
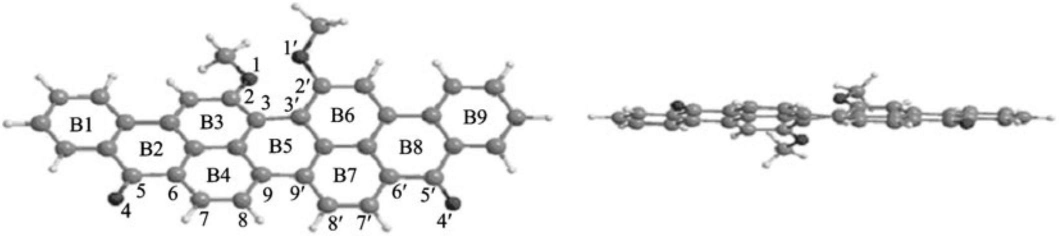
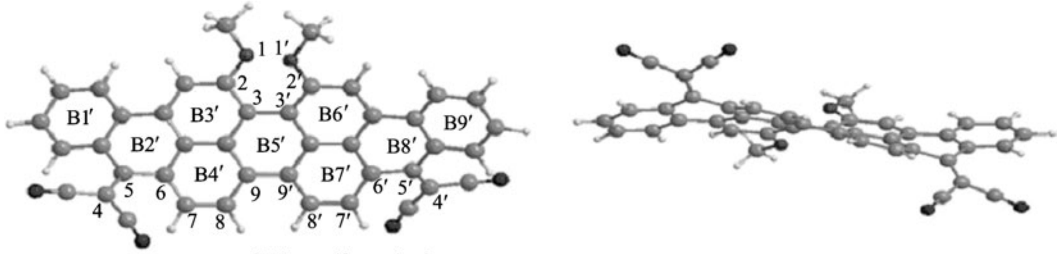


Figure 2 Comparison of ^{1}H NMR spectra between VA-O and VA-CN



compound VA-O (front view)   compound VA-O (side view)



compound VA-CN (front view)   compound VA-CN (side view)

Figure 3 Optimized ground state geometries of VA-O and VA-CN calculated using B3LYP/6-31G (d) in gas.

parameters of dihedral angles are presented in Table 1. It is clear that the nine fused benzene rings in compound VA-O were nearly in the same plane. The distortion between two planes consist of *B*1–*B*4 and *B*6–*B*9 is characterized by dihedral angles labeled with ∠2-3-3′-2′ (31.81°) and ∠8-9-9′-8′ (0.90°). The distortion is mainly attributed to the steric effect of methoxy substitution. Actually, the two methoxy groups are tilted out of these two planes, with ∠1-2-3-3′ (13.07°) and ∠1′-2′-3′-3 (13.04°). In the case of VA-CN, the introduction of the more bulky dicyanomethylene groups leads to even more fiercely twisted ground state geometry. This could be evidenced from the larger dihedral angles of ∠4-5-6-7 (34.23°), ∠4′-5′-6′-7′ (34.21°) and ∠2-3-3′-2′ (33.57°) in VA-CN (Table 1). Consequently, the benzene rings B1′, B2′, B3′ and B4′ are no longer in the same plane, neither are the rings B6′, B7′, B8′ and B9′. Therefore, the chemical environment between aromatic protons ($H_a' - H_g'$ and $H_a'' - H_g''$) becomes different so as to present different chemical shifts in ^{1}H NMR (Figure 2). Based on the same reason, the carbon signals in ^{13}C NMR of VA-CN are also unsymmetrical, and become much more complicated than that of VA-O (as shown in Experimental section).

Table 1 Important dihedral angle parameters optimized ground state geometries of VA-O and VA-CN calculated with B3LYP/6-31G (d) in gas

dihedral angles	VA-O	VA-CN
∠1-2-3-3′	13.07°	11.12°
∠1′-2′-3′-3	13.04°	11.14°
∠2-3-3′-2’	31.81°	33.57°
∠8-9-9′-8’	11.78°	12.04°
∠4-5-6-7	0.90°	34.23°
∠4′-5′-6′-7′	0.90°	34.21°

For VA-CN, the incorporation of dicyanomethylene groups can be further evidenced by IR spectra (Figure 4). Strong peaks at 2925 and 2851 cm^{-1} represent the saturated C-H symmetric and asymmetric flex oscillation, respectively. Due to similar frequency of flex oscillation and low resolution, only two vibration peaks were observed in the spectra. Meanwhile, a weak vibration peak at 750 cm^{-1} correspondes to the characteristically vibrational oscillation of $(CH_2)_n$. In VA-O, the peak at 1740 cm^{-1} is the characteristic peak of carbonyl groups. Notably, after substituted with dicyano-methylene units, the peak at 1740 cm^{-1} disappeared whereas a sharp and strong peak at the wavenumber of 2209 cm^{-1}

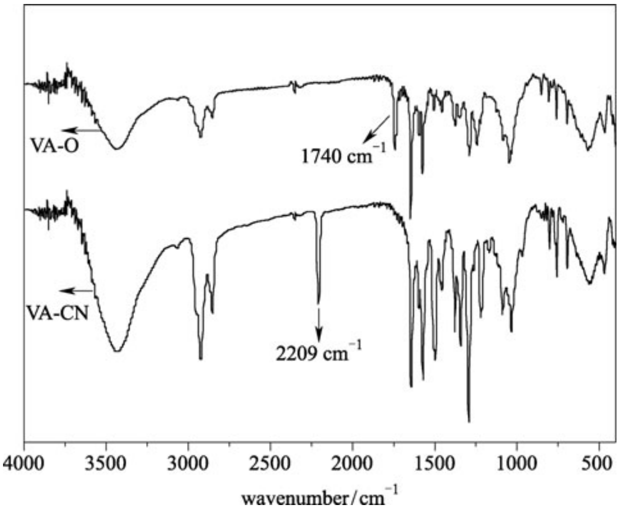


Figure 4 IR spectra of VA-O and VA-CN.

appeared. The new peak corresponds to the characteristic peak of cyano groups in VA-CN. Obviously, two carbonyl groups in VA-O have successfully substituted by the two dicyanomethylene units.

3.2 Photophysical properties of VA-O and VA-CN

The absorption and emission spectra of VA-O and VA-CN in CH_2Cl_2 are shown in Figure 5. The reference compound of VA-O exhibits three absorption peaks at 262, 395 and 648 nm. The λ_{max} at 648 nm is attributed to the intramolecular charge transfer (ICT) band of the violanthrone backbone, which is heavily effected by the charge transfer from *n*-octyloxy groups to carbonyl groups in the violanthrone backbone. Compared with VA-O, when carbonyl groups are substituted with dicyanomethylene groups, a red-shifted absorption peak of VA-CN is observed at 701 nm with higher molar extinction coefficient ($4.69 \times 10^4\ L \cdot mol^{-1} \cdot cm^{-1}$).

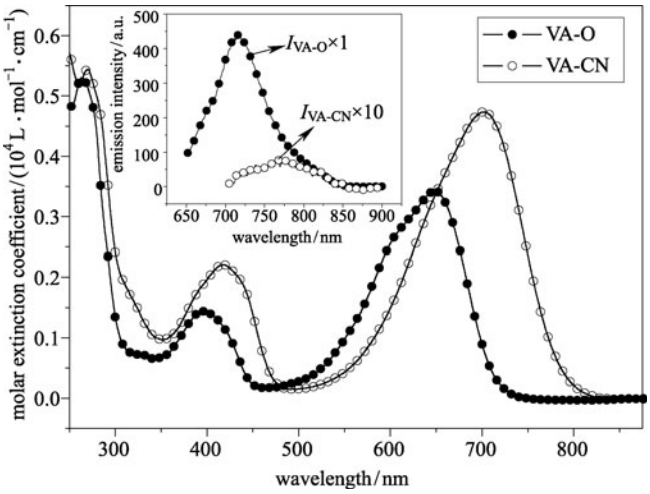


Figure 5 Absorption spectra of VA-O and VA-CN in CH_2Cl_2 ($1.0 \times 10^{-5}\ mol \cdot L^{-1}$). Inset: emission spectra of VA-O (× 1) and VA-CN (× 10).

As is known, the reference carbonyl-containing compound VA-O is a NIR fluorescent chromophore with an emission located at 716 nm and a Stokes-shift (58 nm) in CH_2Cl_2 (Figure 5), resulting from the possible ICT transition from *n*-octyloxy group (electron donor) to carbonyl group (electron acceptor) in the violanthrone backbone. As a NIR fluorescent dye, the emission peak of VA-O is located at 716 nm, which is not far from the visible red light region. Actually, for the purpose of applications in military and anti-counterfeiting, there is a very serious problem in the emission spectra of VA-O from the visible light region, almost 40% in the range of 650 – 700 nm (Figure 5). Generally, the higher ICT effect, the longer redshift. For the purpose of increasing the ICT effect and of shifting the emission wavelength, the higher electron-deficient dicyanomethylene groups are incorporated. As expected, in consistent with the above red-shift in absorption, the emission peak of VA-CN moves to the longer wavelength at 771 nm (Figure 5). However, the emission peak of VA-CN becomes unexpectedly quenched. With respect to VA-O, the observed fluorescence is decreased by roughly 2 orders of magnitude upon the substitution with highly electron-deficient dicyanomethylene groups. Obviously, the serious fluorescence quenching of VA-CN may be resulted from the existence of non-radiative competion before the radiative emission processes [25]. As mentioned above, the conformation of nine fused benzene rings changes from the original planar (VA-O) to the twisted and unsymmetrical (VA-CN) upon the incorporation of dicyanomethylene unit, which might also play a role in the fluorescence quenching.

To further explain the effect of ICT and large red-shift between λ_{abs} and λ_{em}, the solvatochromism was investigated in detail (Figures 6–8). With an increase in the solvent polarity, VA-O presents a 46 nm red-shift from 629 nm in CCl_4 to 675 nm in DMF (Figure 6), and VA-CN red shifts by 27 nm from 679 nm in CCl_4 to 706 nm in DMF (Figure 7). Correspondingly, the solvatochromism in the emission band of VA-O was observed to shift from 681 nm in CCl_4 to 723 nm in DMF (Figure 8). With increasing solvent polarity, the molecule becomes high polarization, thus enlarging the dipole moments and resulting in red-shift in both absorption and emission spectra. The higher the polarity of solvents, the lower the energy of relaxed states, which was arisen from the larger red-shift in the emission spectra for VA-O [26]. However, the solvent polarity does not present significant influence on molar extinction coefficients.

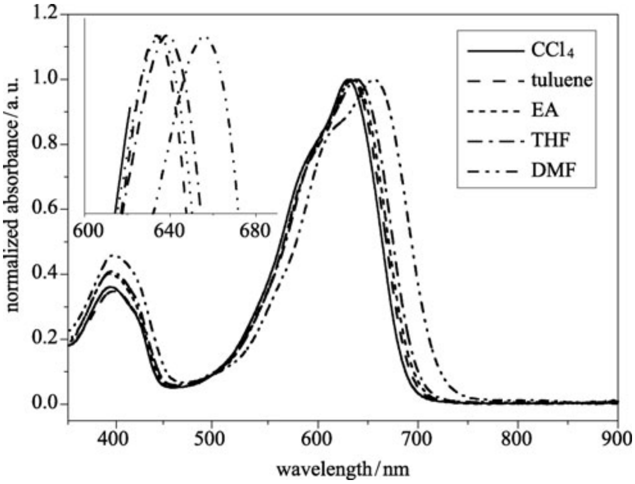


Figure 6 Normalized absorption spectra of VA-O in a variety of solvents.

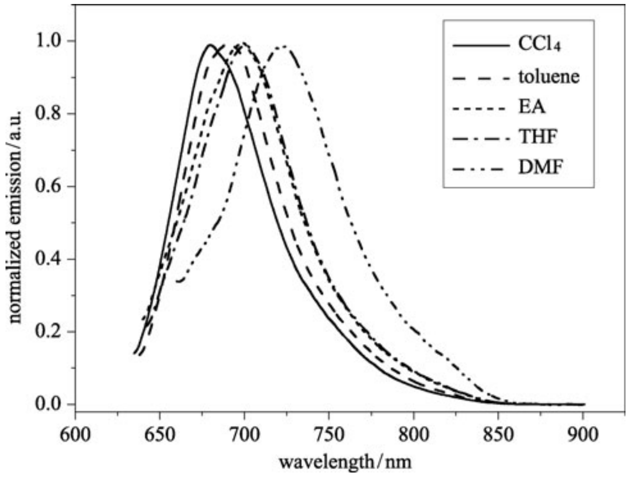


Figure 7 Normalized emission spectra of VA-O in a variety of solvents (excitation at $\lambda_{\max}$).

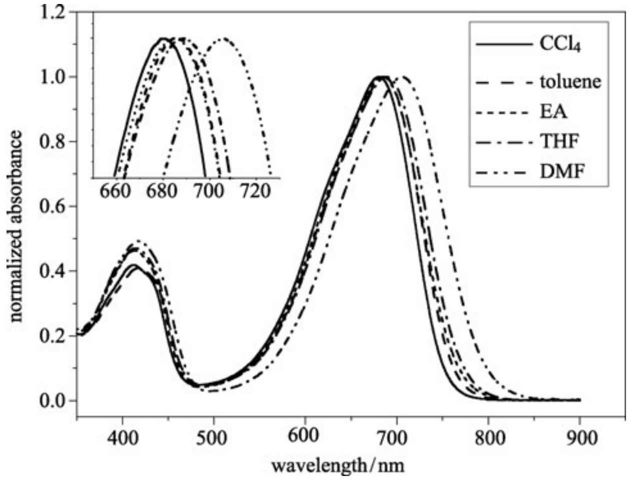


Figure 8 Normalized absorption spectra of VA-CN in a variety of solvents.

3.3 Electrochemical properties of VA-O and VA-CN

To investigate the redox properties, cyclic voltammetry measurements were performed in CH_2Cl_2 at a scan rate of $100\,mV\cdot s^{-1}$ using Pt as working electrode, Ag/AgCl as reference electrode, Pt wire as counter electrode, and ferrocene as the internal standard. The cyclic voltammograms of VA-O and VA-CN were shown in Figure 9. Both VA-O and VA-CN shows two reversible oxidation peaks at potentials of 1.09, 1.49 V and 1.10, 1.49 V vs NHE, respectively, which are assigned as the oxidation of violanthrone backbone. Besides, VA-O presents a single reversible reduction peak at −0.96 V vs NHE, which can be attributed as the reduction of carbonyl groups into the quinonoidal dianion [27]. Comparing with VA-O, the reduction potential of VA-CN was shifted to −0.56 V vs NHE due to stronger electron deficiency resulted from the dicyanomethylene group. It is the ICT effect of stronger electron-withdrawing dicyanomethylene unit that decreases the LUMO energetic stabilization from the stronger electron-withdrawing capability of dicyanomethylene group with respect to carbonyl group, resulting in a band gap contraction from 1.82 eV (VA-O) to 1.50 eV (VA-CN). Obviously, the analysis of redox potentials reveals the importance of carbonyl and dicyanomethylene groups in modulating the frontier molecular orbital of VA-O and VA-CN with good reversibility (redox stability).

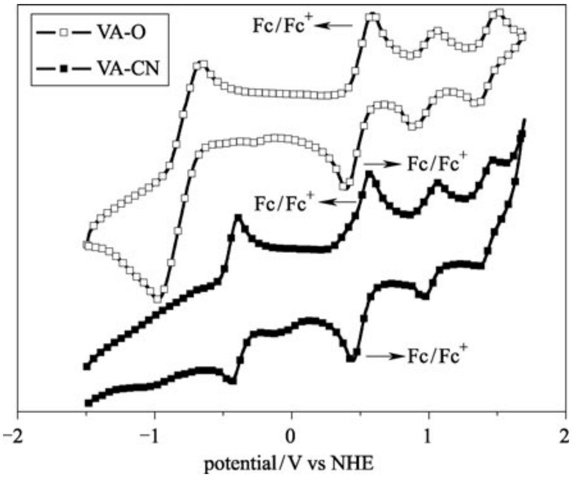


Figure 9 Cyclic voltammograms of VA-O and VA-CN in CH_2Cl_2 ($1.0\times10^{-3}\,mol\cdot L^{-1}$).

We also calculated the solvent effect on the electronic property of compound VA-CN by hybrid density functional theory with 6–31G* basis set as implemented in the Gaussian 03 program [17]. As seen in Table 2, both LUMO and HOMO are destabilized upon the increase of polarity. The decrease of the band gap, which is due to the bathochromic solvent effect, is observed since the HOMO destabilization is the major effect. This trend is in good agreement with experiments.

Table 2 Calculated HOMO, LUMO, and band gap (HOMO and LUMO gaps) of VA-CN

	vacuum	CCl_4	DMF
LUMO (eV)	−3.5242	−3.4822	−3.4558
HOMO (eV)	−5.3541	−5.2678	−5.1881
Band gap (eV)	1.8299	1.7856	1.7323

3.4 Interaction of VA-CN with electron-rich amine

Considering the low reduction potential (−0.56 V vs NHE), VA-CN might be considered as a good electron acceptor because of the stronger electron deficiency resulted from dicyanomethylene group. We attempted to utilize amine as potential donor to get further insight into the binding with VA-CN. Upon titrating with *n*-butyl amine, the absorption spectra of VA-CN shows an obvious decrease at the peak of 701 nm and an increase at the peak of 633 nm with a distinct isosbestic point at 654 nm (Figure 10). Due to the low reduction potential, it is possible to expect that the system of VA-CN with strong electron-deficient cyano groups could bind with lone pair electrons of amine and thus could result in a possible intermolecular charge transfer band (located at 633 nm). After binding with amines, the original intramolecular charge transfer band becomes decreased, thus resulting in the absorption peak ($\lambda_{\max}$) blue-shifted by 68 nm from 701 to 633 nm. Moreover, the absorption can be recovered to the original state while equivalent acetic acid was added. In order to further avoid the interference of hydrogen bond, appropriate amount methanol was added into the solvent followed by *n*-butyl amine. Same change in the absorption blue-shift is kept. Therefore, possible hydrogen bonding might be ruled out.

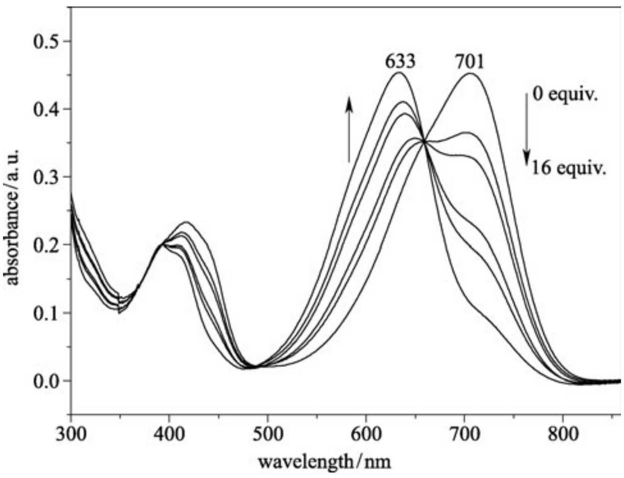


Figure 10 UV-Vis spectra of VA-CN with various equivalent of *n*-butyl amine in CH_2Cl_2 (1.0×10^{-5} mol·L^{-1}).

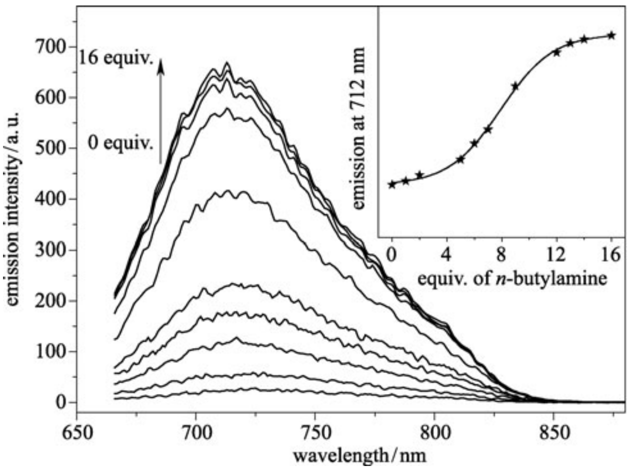


Figure 11 Emission intensity at 712 nm of VA-CN with various equivalence of *n*-butyl amine in CH_2Cl_2 (1.0×10^{-5} mol·L^{-1}).

More interestingly, a distinctive increase of fluorescence excited at the isosbestic point of 654 nm was found upon the addition of various equivalent of *n*-butyl amine (Figure 11). The fluorescence intensity was increased by nearly 30 folds. Also, the fluorescence "*off-on*" is reversible. While the addition of acetic acid, the fluorescence intensity decreases accordingly, which was indicative of the possible interaction between the deficient center of VA-CN and lone-pair electrons of amine. It shows that VA-CN might be served as a promising fluorescent sensor for electron-rich amines.

4 Conclusions

A novel NIR dye VA-CN was synthesized and fully characterized by ^{1}H NMR, HRMS, and IR spectra. Upon the incorporation of two strong electron-withdrawing dicyanomethylene units, the original planar conformation of violanthrone ring becomes twisted and unsymmetrical. It is demonstrated that VA-CN could be considered as a good electron acceptor due to its stronge electron deficiency resulted from the dicyanomethylene group. A distinct increase in fluorescence was observed with 30-fold upon the addition of *n*-butyl amine. The reversible fluorescence "*off-on*" shows that VA-CN might be served as a promising fluorescent sensor for electron-rich amines.

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