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Stabilization of the *E/Z* Configuration for Cyanostilbene-based Luminogens by Enhanced Charge Transfer Excited State

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Abstract: The *E/Z* isomerization reaction is found extensively in most organic molecules containing double bond unit. This limits their practical application as luminescent materials partly, especially under photoirradiation. Therefore, it is important to obtain *E/Z* isomers with stable configuration in the excited state after photoirradiation. It is well known that cyanostilbene and its analogues play an important role in the development of organic opto/electronic materials. The substituted cyano group on C=C double bonds has strong electron-withdrawing ability and large steric hindrance, which benefits the formation of donor-acceptor (D-A) structures and formation of intramolecular charge transfer. In our previous work, we reported a triphenylamine-cyanostilbene molecule (TPNCF) formed by modifying the cyanostilbene structure with triphenylamine, which maintained a stable *E/Z* configuration as a film and in high polar solvents. According to solvatochromism mechanisms and the results of theoretical calculations, we proposed that the charge transfer (CT) excited state between the triphenylamine donor and cyanostilbene acceptor groups induced the stable configuration of the *E*- and *Z*- isomers under photoirradiation. Under irradiation, the *E/Z* isomerization process occurring at a higher energy locally excited (LE) state was suppressed by a rapid internal conversion process from the LE to CT state. This work inspired us to provide a universal and effective molecular design strategy by modifying D-A substituents on double bonds that can successfully stabilize *E/Z* isomers. To further confirm that the CT excited state induced stable *E*- and *Z*- isomers in the cyanostilbene structure under photoirradiation, we designed and synthesized a donor-acceptor phenoxazine-cyanostilbene molecule (PZNCF) and successfully characterized its two *E/Z* isomers. In comparison with the reported TPNCF molecule, the *in-situ* NMR and UV spectra of *E*- and *Z*- isomers of PZNCF demonstrated that the *E/Z* isomerization rate became slower under photoirradiation, which indicated that the stronger electron-donating group of phenoxazine substituted in the cyanostilbene structure induced a more stable *E/Z* isomer configuration in its excited state. DFT calculations and photophysical results indicated that a stronger CT state was generated in both *E*- and *Z*- isomers of PZNCF. This further confirmed our hypothesized mechanism where the stable *E/Z* configuration can be obtained under photoirradiation by forming a suitable donor-acceptor structure to suppress the *E/Z* isomerization reaction in the LE state by a rapid internal crossing process from the LE to CT state. This molecular design strategy is of great significance to organic photochemistry and photoelectronics for molecules with double bond units.

Key Words: *E/Z* configuration; Charge transfer excited state; Cyanostilbene; Donor-acceptor structure; Locally excited state

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通过增强电荷转移激发态构建激发态下稳定的基于氰基二苯乙烯的 *E/Z* 构型

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摘要: 在前期工作中, 我们报道了一个三苯胺基团链接氰基二苯基乙烯单元的分子TPNCF, 并认为从局域激发态到电荷转移(CT)激发态的快速内转换, 能够有效抑制*E/Z*异构化反应。为了进一步证明CT态能够诱导*E/Z*构型的稳定, 本文中我们将三苯胺基团替代为给电子能力更强的吩噻嗪基团, 设计合成了分子PZNCF, 并且成功获得其*E/Z*异构体。通过对原位核磁及紫外光谱数据的分析, 我们发现相比于TPNCF, PZNCF在光辐照下的*E/Z*异构化反应明显变慢。这说明对于氰基二苯基乙烯单元, 一个更强给电子能力基团吩噻嗪的引入能够使其在激发态下具有更稳定的*E/Z*构型。密度泛函理论计算及光物理测试结果表明PZNCF分子具有较强的电荷转移激发态, 这也更加证实了我们先前的结论: 通过合理构建给受体结构, 能够获得激发态下构型稳定的*E/Z*异构体。

关键词: *E/Z*构型; 电荷转移激发态; 氰基二苯基乙烯; 给受体结构; 局域激发态

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1 Introduction

The *E/Z* isomerization reaction is nearly unavoidable under the photo-irradiated conditions in most of the organic molecules containing the double bond unit^{1,2}. To evaluate the role of *E/Z* isomerization in photophysical process, some nice and impressive research works related to *E*- and *Z*- isomers have been reported³⁻¹⁰. Especially, a series of *E*- and *Z*- isomers based on the tetraphenylethylene structure linked with large volume or long chains have been reported to investigate the aggregation-induced emission (AIE)¹¹ generation mechanism¹²⁻¹⁷. However, all these reported *E*- and *Z*- isomers still underwent the rapid *E/Z* isomerization reaction under the photo irradiation according to their reported data³⁻²⁰. Therefore, it is still important and inevitable to obtain the *E*- and *Z*- isomers with stable configuration in the excited state under photo irradiation, which is of great significances to understand the intrinsic photophysical property.

Recently, we reported the pure *E*- and *Z*- two isomers of a D-A molecule TPNCF (triphenylamine-cyanostilbene molecule) based on triphenylamine (TPA) and cyanostilbene (CNS) moieties, which could keep their stable *E/Z* configurations under photo irradiation²¹. And it is found that the lowest charge transfer (CT) excited state (*S*₁) between triphenylamine donor and cyanostilbene acceptor groups gradually reduced in energy, which effectively suppressed the *E/Z* isomerization reaction at the higher-energy *S*₂ state owing to the rapid internal crossing process from *S*₂ state to *S*₁ state, was the essential reason for the observed stable *E/Z*-isomers under photo irradiated condition.

In order to further investigate it, herein we designed a new donor-acceptor molecule PZNCF (phenoxazine-cyanostilbene molecule) with a stronger electron-donating group of phenoxazine to replace the previous triphenylamine group, and the pure two isomers *E*-PZNCF and *Z*-PZNCF were both

obtained. NMR spectra and photophysical properties demonstrated a fact that the *E/Z* isomerization rate in the case of *E*-PZNCF and *Z*-PZNCF became slower than that of *E*-TPNCF and *Z*-TPNCF under photo irradiation, which indicated the stronger electron donating group of phenoxazine substituted in cyanostilbene structure induced a more stable *E/Z* isomer configuration in its excited state. Density functional theory (DFT) calculation and photophysical results indicated that a stronger charge transfer state was generated in both *E*- and *Z*- isomers of PZNCF. These further confirmed our previous mentioned mechanism, that is, the stable *E/Z* configuration under photo irradiation could be obtained through constructing a reasonable donor-acceptor structure with the CT state. Thereby, we focus on providing a deep and general understanding of substituted double bond unit to pave the way to further rational structural design for all kinds of organic molecules containing the double bond unit.

2 Experimental and computational

2.1 Materials and methods

All the reagents or chemicals were commercial and analytical products without further purification. ¹H (500 MHz) NMR spectra of the synthesized compounds were recorded on Bruker AVANCE III instrument (Bruker, Switzerland). ¹³C (400 MHz) NMR spectra of the synthesized compounds were recorded on Bruker Advance III instrument (Bruker, Switzerland). Mass spectra (MALDI-TOF-MS) analysis was recorded using an AXIMA-CFRTM plus instrument (Shimadzu, Japan). Mass spectra (ESI-MS) analysis was recorded using a ThermoFisher LCQTM Deca XP plus and Agilent 1200-6210 instrument (Agilent, America). Photophysical properties were investigated by a Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) and a Perkin-Elmer LS-55 luminescence spectrophotometer (the

integration time were set to be 0.01 s in order to shorten the measurement time to be less than 20 s). The photo irradiation was carried in a ZF-20D ultraviolet analyzer (YUHUA, China) with a UV light (365 nm, 24 W). Electrochemical measurements were conducted by a CHI660E electrochemical analyzer (Chenhua, China), with glassy carbon as the working electrode, platinum wire as the auxiliary electrode and Ag/Ag⁺ as the reference electrode, 0.1 mol·L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) dissolved in acetonitrile was employed as the supporting electrolyte.

2.2 Synthesis of 2-(4-(10H-phenoxazin-10-yl)phenyl)acetonitrile

In a dry nitrogen atmosphere, a mixture of phenoxazine (0.37 g, 2.0 mmol), 4-bromophenylacetonitrile (0.47 g, 2.4 mmol), tri-*tert*-butylphosphine (0.11 g, 0.52 mmol), palladium acetate (0.03 g, 0.12 mmol) and sodium *tert*-butoxide (0.50 g, 5.2 mmol) in 30 ml toluene was heated under 115 °C for 24 h^{22,23}. After the reaction, the mixture was cooled to room temperature and quenched with water and extracted with chloroform. The combined organic layer was washed with distilled water three times and dried over anhydrous magnesium sulfate. Then the solvent was evaporated in a vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1/3 *V/V*) as the eluent to obtain the product as a white solid (0.60 g, 50%). ¹H NMR (500 MHz, CDCl₃) δ (TMS) 7.59 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 6.74–6.57 (m, 6H), 5.90 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 2H, alkyl-H). ESI-MS (mass *m/z*): 297.1 [M – H][–], C₂₀H₁₄N₂O calc. 298.34.

2.3 Synthesis of E-PZNCF and Z-PZNCF

To a mixture of 2-(4-(10H-phenoxazin-10-yl)phenyl)acetonitrile (0.30 g, 1 mmol) and 4-(trifluoromethyl)benzaldehyde (0.17 g, 1 mmol) in 10 ml ethanol, sodium hydroxide (0.04 g, 1 mmol) was added. The mixture was heated under 45 °C for 24 h, then cooled to room temperature and filtered. The residue was washed with cold ethanol by three times, and further purified by column chromatography *via* eluent (CH₂Cl₂/*n*-hexane: 4/1, *V/V*) to obtain the products as a yellow solid and an orange solid.

(*E*)-2-(4-(4a,5a,9a,10a-tetrahydro-10H-phenoxazin-10-yl)phenyl)-3-(4-(trifluoromethyl)phenyl)acrylonitrile (*E*-PZNCF). Yellow solid, 0.03 g, yield: 6%. ¹H NMR (500 MHz, CDCl₃) δ (TMS) 7.61 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.50 (s, 1H, vinyl-H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 6.74–6.70 (m, 4H), 6.70–6.64 (m, 2H), 5.96 (d, *J* = 8.9 Hz, 2H). ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ 143.99, 143.04, 136.73, 133.72, 132.05, 131.90, 131.66, 129.87, 125.75, 125.67, 123.68, 121.85, 119.14, 116.01, 115.73, 113.13, 31.44, 30.18. MALDI-TOF MS (mass *m/z*): 455.5 [M + H]⁺, C₂₈H₁₇F₃N₂O calc. 454.44.

(*Z*)-2-(4-(4a,5a,9a,10a-tetrahydro-10H-phenoxazin-10-yl)phenyl)-3-(4-(trifluoromethyl)phenyl)acrylonitrile (*Z*-PZNCF). Orange solid, 0.39 g, yield: 85%. ¹H NMR (500 MHz, CDCl₃) δ (TMS) 8.05 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.79 (d,

J = 8.4 Hz, 2H), 7.68 (s, 1H, vinyl-H), 7.51 (d, *J* = 8.5 Hz, 2H), 6.77–6.67 (m, 4H), 6.64 (t, *J* = 8.4 Hz, 2H), 5.98 (d, *J* = 9.2 Hz, 2H). ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ 142.92, 140.06, 139.52, 135.67, 132.88, 130.78, 128.49, 127.83, 125.04, 125.00, 122.27, 120.74, 116.14, 114.66, 112.43, 112.17, 76.19, 17.42. MALDI-TOF MS (mass *m/z*): 455.1 [M + H]⁺, C₂₈H₁₇F₃N₂O calc. 454.44.

3 Results and discussion

3.1 Design and synthesis

In order to achieve a stronger charge transfer state, the new donor-acceptor molecules *E*-PZNCF and *Z*-PZNCF were designed with phenoxazine to replace the previous triphenylamine group of *E*-TPNCF and *Z*-TPNCF (Fig. 1),

3.2 Crystal structure

By the slow diffusion of methanol vapour into a chloroform solution of compounds, we successfully obtained the single crystal of *Z*-PZNCF suited for X-ray structural analysis. The crystal structure clearly demonstrated the *Z* configuration of *Z*-PZNCF and a desirable large twist angle of ~85° was also observed between the nearly planar phenoxazine and the adjacent phenyl in cyanostilbene (Fig. 2). This large twist angle might effectively break the conjugation between the donor phenoxazine and acceptor cyanostilbene, benefit to the

Fig. 1 The *E/Z* isomer molecular structures of TPNCF and PZNCF as well as the detailed synthesis route of *E*-PZNCF and *Z*-PZNCF.

Fig. 2 The single crystal structure of *Z*-PZNCF molecule (CCDC No. 1845093).

generation of charge transfer transition between them, and thus contribute much to the stability of *E/Z* configuration based on our research results.

3.3 UV and PL spectra

The UV and PL spectra were measured firstly for *E*-PZNCf and *Z*-PZNCf, with those of *E*-TPNCf and *Z*-TPNCf as reference, as shown in Fig. 3. The UV spectra of *E*-PZNCf and *Z*-PZNCf exhibited a red-shifted broad absorption band with $\lambda_{\max}$ at 415 and 430 nm respectively in comparison to those of corresponding *E*-TPNCf ($\lambda_{\max} = 380$ nm) and *Z*-TPNCf ($\lambda_{\max} = 398$ nm). Considering the nearly no conjugation between phenoxazine and cyanostilbene, these large redshift of UV spectra should be attributed to the generation of lower-energy charge transfer transition in *E*-PZNCf and *Z*-PZNCf. Thus it was reasonable that the PL spectra of *E*-PZNCf ($\lambda_{\max} = 620$ nm) and *Z*-PZNCf ($\lambda_{\max} = 615$ nm) displayed also large redshifts of ~ 100 nm in comparison with those of *E*-TPNCf ($\lambda_{\max} = 528$ nm) and *Z*-TPNCf ($\lambda_{\max} = 512$ nm), due to the formation of lower-energy charge transfer emission in *E*-PZNCf and *Z*-PZNCf. The lower-energy charge transfer state in *E*-PZNCf and *Z*-PZNCf possessed the much lower fluorescent quantum efficiencies of $(4 \pm 3)\%$ and $(9 \pm 3)\%$ respectively in solution, which should be ascribed to the introduction of phenoxazine with stronger electron-donating ability and lower ionization energy. And in the common solvents such as chloroform, tetrahydrofuran, and acetonitrile, nearly none emission could be observed for both *E*-PZNCf and *Z*-PZNCf, which might reflect the stronger charge transfer state induced by phenoxazine in *E*-PZNCf and *Z*-PZNCf than those in *E*-TPNCf and *Z*-TPNCf.

3.4 Electrochemistry

The electrochemical properties of *E*-PZNCf and *Z*-PZNCf were investigated to evaluate their electronic energy levels *via* cyclic voltammetry method, with those of *E*-TPNCf and *Z*-TPNCf as reference, as shown in Fig. 4. We could find that *E*-PZNCf and *Z*-PZNCf exhibited nearly the same redox properties, and the redox peaks in the negative potential range were similar to those of *E*-TPNCf and *Z*-TPNCf, but To confirm the charge transfer excited state properties of much

lower onset oxidation potentials (0.78 and 0.76 V) were observed for *E*-PZNCf and *Z*-PZNCf in comparison with those (0.92 and 0.94 V) of *E*-TPNCf and *Z*-TPNCf. Then the highest occupied molecular orbitals (HOMO) of *E*-PZNCf and *Z*-PZNCf were roughly calculated to be -5.15 and -5.13 eV, higher than those of *E*-TPNCf and *Z*-TPNCf (-5.29 and -5.31 eV), confirming the stronger electron-donating ability and lower ionization energy of phenoxazine which would induce the stronger charge transfer state in *E*-PZNCf and *Z*-PZNCf.

3.5 DFT analysis

To confirm the charge transfer excited state properties of *E*-PZNCf and *Z*-PZNCf, theoretical calculation of electronic orbital distribution and energy level were carried out by B3LYP method. As shown in Fig. 5, DFT analysis demonstrated that the highest occupied molecular orbitals (HOMO) of *E*-PZNCf and *Z*-PZNCf were mainly located at the phenoxazine part, while their lowest unoccupied molecular orbitals (LUMO) were completely distributed at cyanostilbene part. The totally separate HOMO and LUMO distribution indicated the pure charge transfer character in the excited state for both *E*-PZNCf and *Z*-PZNCf. Compared with the HLCT character^{24,25} for *E*-TPNCf and *Z*-TPNCf which contained both a major part of CT transition from triphenylamine to cyanostilbene unit and a minor part of LE transition of cyanostilbene, it was obvious the pure CT transition in *E*-PZNCf and *Z*-PZNCf was much stronger. And the calculated energy level of HOMOs were around -4.8 eV for both *E*-PZNCf and *Z*-PZNCf, much higher than those of *E*-TPNCf and *Z*-TPNCf (-5.1 eV), which were consistent with the electrochemical results, further indicating the stronger charge transfer state in *E*-PZNCf and *Z*-PZNCf.

3.6 *E/Z* configuration stability

The *E/Z* configurations of *E*-PZNCf and *Z*-PZNCf isomers could be confirmed by the characteristic chemical shifts of their original NMR spectra in deuterated chloroform (CDCl_3). The special single peaks corresponding to the vinyl hydrogen atom of pure *E*-PZNCf and *Z*-PZNCf were located at δ 7.50, 7.68 respectively, which were consistent with those of *E*-TPNCf and *Z*-TPNCf at δ 7.38, 7.61 respectively in CDCl_3 . Unlike the

Fig. 3 The UV and PL spectra of *E*-PZNCf and *Z*-PZNCf in toluene at $10 \mu\text{mol}\cdot\text{L}^{-1}$ with those of *E*-TPNCf and *Z*-TPNCf as reference.

Fig. 4 The cyclic voltammetry electrochemical curves of *E*-PZNCf and *Z*-PZNCf molecules with those of *E*-TPNCf and *Z*-TPNCf as reference.

Fig. 5 The electron cloud distribution of electronic orbitals HOMO and LUMO for optimized *E*-PZNCF and *Z*-PZNCF molecules.

chemical shifts of triphenylamine at δ 7.0–7.4 in *E*-TPNCF and *Z*-TPNCF, those of phenoxazine in *E*-PZNCF and *Z*-PZNCF were located at δ ~6.0–6.8, far away from those chemical shifts of cyanostilbene, which made it easy to observe the change of chemical shifts in *E/Z* isomerization.

After the photo irradiation for 30 min, the *in-situ* NMR spectra of *E*-PZNCF and *Z*-PZNCF in CDCl_3 and DMSO-d_6 were measured to evaluate the *E/Z* isomerization in their cases, as shown in Fig. 6. Similar to *E*-TPNCF and *Z*-TPNCF, the NMR spectra of *E*-PZNCF and *Z*-PZNCF in high polar DMSO-d_6

remained unchanged after photo irradiation for 30 min (Fig. S1, Supporting Information). Surprising to us was that *E*-PZNCF and *Z*-PZNCF kept also stable without any *E/Z* isomerization observed in the relatively lower polar CDCl_3 solvent (Fig. 6b), in which *E*-TPNCF and *Z*-TPNCF converted to each other quickly with large amounts (Fig. 6a). This obviously indicated that *E*-PZNCF and *Z*-PZNCF were much more stable in the *E/Z* configuration in comparison with *E*-TPNCF and *Z*-TPNCF under the photo irradiated conditions.

In order to further investigate the *E/Z* isomerization or configuration stability in different polar solvents for *E*-PZNCF and *Z*-PZNCF, their *in-situ* UV spectra under different photo irradiation time were measured. As shown in Fig. S2 (Supporting Information), the original UV spectra of *E*-PZNCF showed the obvious blueshifts of ~10–20 nm in peak position compared to *Z*-PZNCF in all the polar solvents, and as the increase of solvents polarity, the isomerisation process of PZNCF became obviously slower in rate with more irradiation time to reach the equilibrium, which was similar to those of *E*-TPNCF and *Z*-TPNCF. In the low polar hexane solvent (Fig. S2a, Supporting Information), we could found that the UV spectra of *E*-PZNCF and *Z*-PZNCF started to move on the contrary once under UV irradiation, indicating the happen of *E/Z* isomerization reaction between them, which quickly reach the equilibrium in 5 min.

Fig. 6 The original and *in-situ* NMR spectra under photo irradiation of UV light (365 nm) for 30 minutes in deuterated chloroform (CDCl_3) of (a) TPNCF isomers and (b) PZNCF isomers.

Fig. 7 The *in-situ* UV spectra of a) *E*-TPNCF and *Z*-TPNCF as well as b) *E*-PZNCF and *Z*-PZNCF under different photo irradiated time of UV light (365 nm) in diethyl ether.

While the experiments were conducted in high polar acetonitrile solvent (Fig. S2c, Supporting Information), their UV spectra even did not move a little. However, it is worth mentioning that the *E/Z* isomerization reaction in the cases of *E*-PZNCf and *Z*-PZNCf became much slower at rate than those in *E*-TPNCf and *Z*-TPNCf isomers. As shown in Fig. 7, the *E/Z* isomerization reaction of *E*-TPNCf and *Z*-TPNCf isomers happened quickly and reached the equilibrium in 5 min in the moderate-polar diethyl ether solvent, while that of both *E*-PZNCf and *Z*-PZNCf became obviously slower at rate without reaching the equilibrium in 120 min under photo irradiation. Except for the solvent polarity capable of controlling the *E/Z* isomerization reaction rate in the excited state, molecular structural change could also achieve to enhance the stability of their *E/Z* configurations. These results further demonstrated that the introduction of a stronger electron-donating phenoxazine helped to restrain the *E/Z* isomerization reaction, which might be ascribed to the stronger charge transfer excited state derived from the introduction of much stronger donor phenoxazine in the cases of *E*-PZNCf and *Z*-PZNCf.

4 Conclusions

We synthesized the donor-acceptor phenoxazine-cyanostilbene isomers and studied their configuration stability in comparison with our reported triphenylamine-cyanostilbene. Their spectroscopy investigation demonstrated a stronger donor can help to stabilize their *E/Z* configuration. The results provide a strong evidence for our previous mentioned mechanism that *E/Z* isomerization reaction in cyanostilbene structure can be effectively restrained at excited state by modify donor-acceptor structure. This guideline should be further developed in other molecular structural design with double bond to achieve more configuration-stable molecules for organic photo-electronic applications.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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