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An aggregation-induced emissive chromophore as a ratiometric fluorescent sensor for cyanide in aqueous media

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ABSTRACT

A *para*-terphenyl derivative containing a lateral diphenylamino group and two terminal dicyanovinyl groups has been designed and synthesized. This compound displays aggregation-induced emission characteristics and thus shows intense intramolecular charge transfer fluorescence even in the condensed state, including in the aggregates formed in an aqueous solvent system consisting of greater than 99% water and in the solid state. The addition of cyanide to its aggregates in aqueous media induces a large blue shift in fluorescence, enabling ratiometric fluorescence sensing of cyanide anions. In addition, its prompt fluorescence responses to cyanide anions were also observed even in the solid state.

1. Introduction

The sensitive and selective recognition of anions has attracted significant consideration because of their indispensable roles in biological, environmental, and industrial processes.[1] Among various anions, cyanide detection is particularly important due to its extreme toxicity in physiological systems[2] and the increasing environmental concern caused by its widespread industrial uses in petrochemical, gold mining, photographic, and steel manufacturing.[3] To detect cyanide anions, fluorescence sensing is one of the most powerful methods owing to its simplicity and high sensitivity. The conventional fluorescence methodology, which monitors the fluorescence intensity at a single wavelength, is easily interfered by sensor concentration, photobleaching, and illumination intensity. To eliminate these effects, it is desirable to develop a ratiometric fluorescent measurement, which uses the ratio of the fluorescent intensities at two different wavelengths, allowing precise and quantitative analysis and imaging even in complicated systems. Although a variety of fluorescent cyanide sensors have been developed based on reversible binding and reaction-based approaches,[4,5] the ratiometric fluorescent ones are still quite limited.[6] Another problem encountered in the fluorescent sensing of cyanide is that most of the fluorescent sensors only function in either pure organic solvents or solutions containing a large amount of organic solvent, significantly rare in aqueous media.[7] In this regard, it is still very challenging to obtain ratiometric fluorescent sensor for cyanide, which can be used in aqueous media.

To realize the ratiometric fluorescent sensing of cyanide in aqueous media, one major obstacle is that most organic fluorophores suffer from the aggregation-induced fluorescence quenching phenomenon and are weakly emissive or even non-emissive in water as a result of the aggregates formation. So it is desirable to design the cyanide active fluorophores, which exhibit the aggregation-induced emission characteristics and are highly emissive in aqueous phase despite the formation of aggregates.[8–10] Herein we designed a new cyanide sensor **1**, a lateral diphenylamino substituted *para*-terphenyl derivative with two dicyanovinyl groups attached at the terminal positions (Fig. 1). In this molecular design, we chose the lateral diphenylamino-substituted *para*-terphenyl system since it has been proved to be an effective strategy to attain intense fluorescence in the condensed state by introduction

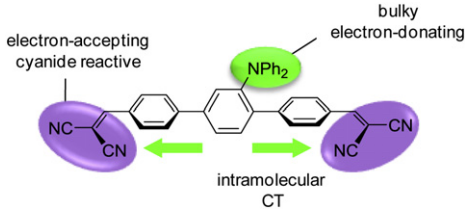

Fig. 1. Molecular design concept of **1**.

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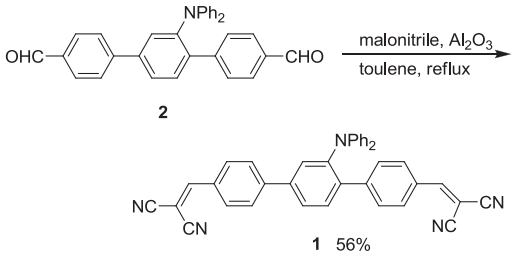
of the bulky electron-donating diphenylamino group at the side position of an electron-accepting *para*-terphenyl framework.[11] The dicyanovinyl group was introduced because it can act not only as a strong electron-accepting group to induce an intramolecular charge transfer (ICT) transition but also as a cyanide reactive unit.[12] We envisioned that this molecule would display intense ICT fluorescence even in the aggregates formed in an aqueous media. The nucleophilic attack of cyanide to the α-position of the dicyanovinyl group would disrupt the ICT transition and lead to significant changes in fluorescence, enabling the ratiometric fluorescent sensing of cyanide. We indeed found that compound **1** displays intense fluorescence and prompt ratiometric fluorescent responses to cyanide in an aqueous solvent system consisting of greater than 99% water. Moreover, its intense fluorescence and prompt fluorescence responses to cyanide were also observed even in the solid state.

2. Results and discussion

2.1. Synthesis

Compound **1** was easily synthesized via a one-step reaction as depicted in Scheme 1. In the presence of basic aluminum oxide, the condensation of malononitrile with compound **2**, which was previously prepared through Pd(0)-catalyzed Suzuki–Miyaura coupling of 2,5-dibromo-*N*,*N*-diphenylaminobenzene with *para*-formylphenylboronic acid,[11] provided **1** as yellowish orange solids in 56% yield. Its structure was fully characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and high-resolution mass spectrometry.



Scheme 1. Synthesis of **1**.

2.2. Photophysical properties

The UV/vis absorption and emission spectra of **1** are shown in Fig. 2 and the related data are summarized in Table 1. In cyclohexane, the absorption of **1** features a much weaker band at the longer wavelength (λ_{abs}=448 nm, ε=2273 M^{-1} cm^{-1}) relative to the intense band at 355 nm (ε=32,350 M^{-1} cm^{-1}). In the fluorescence spectra, **1** exhibits an intense emission at 543 nm with a high quantum yield (Φ_F=0.56). It is notable that a large solvatochromism was observed in fluorescence (λ_{em}=543 nm in cyclohexane; 568 nm in benzene; 585 nm in $CHCl_3$; 589 nm in THF) while the absorption spectra display trivial solvent dependence. In addition, the large bathochromism in emission is accompanied by a significant decrease of the fluorescence efficiency with the increasing solvent polarity. And thus the fluorescence in THF (Φ_F=0.0015) is almost invisible to the naked eyes and in MeCN is not detectable even by the spectrometer. These facts clearly suggest a higher polarity in excited state than in the ground state.

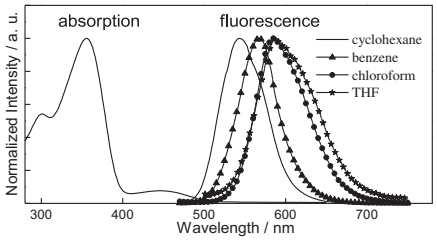


Fig. 2. UV/vis absorption and fluorescence spectra of **1**.

Table 1
UV/vis absorption and fluorescence data of **1** in various solvents

Solvent	λ_{abs} (nm)[a]	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_F[b]
Cyclohexane	448	2273	543	0.56
Benzene	446	407	568	0.18
$CHCl_3$	458	304	585	0.0047
THF	442	402	589	0.0015
MeCN	442	1462	n.d.[c]	n.d.[c]

[a] Only the longest maxima are shown.
[b] Calculated using Rhodamine B as standard.
[c] Not detected.

To elucidate the influence of the geometric and electronic structure of **1** on photophysical properties, we conducted theoretical calculations. The optimizations of the molecular geometry were carried out using density-functional theory (DFT) at the B3LYP/6-31G(d) level of theory. We also performed time-dependent density-functional theory (TD-DFT) calculations at the B3LYP/6-31G(d) theory. The optimized molecular structure and the pictorial drawing of the molecular orbitals are shown in Fig. 3 and Fig 4, respectively.

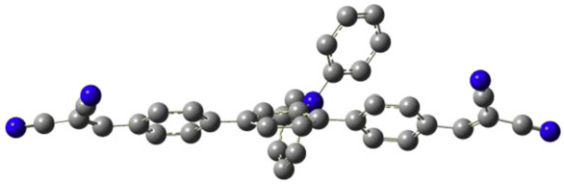


Fig. 3. Optimized structure of **1** calculated at B3LYP(6-31G(d)) theory.

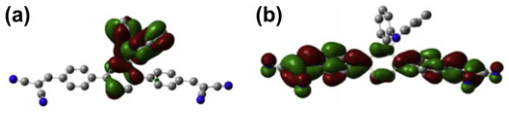


Fig. 4. Pictorial drawings of (a) HOMO and (b) LUMO of **1** calculated at B3LYP/6-31G(d) theory.

As shown in Fig. 3, the terphenylene moiety of **1** shows a non-planar main chain structure, similar to that of the single crystal X-ray structure of other lateral diphenylamino-substituted terphenyl derivatives.[11] The dihedral angles between the two terminal benzene rings and the central benzene ring are 34.9° and 47.6°, respectively. Apparently, the difference in the dihedral angles arises from the difference in the steric congestion between the two terminal benzene rings and the central benzene ring. Owing to the twisted main chain structure and the steric hindrance of the lateral diphenylamino group, it is presumed that the molecules of **1** in the condensed state would be far apart from each other, suppressing intermolecular interactions. Another notable feature for the optimized structure of **1** is that the terminal dicyanovinyl groups are almost completely coplanar with the attached benzene rings, suggesting the possible effective conjugation between the