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Synthesis and self-assembly of luminescent hexacatenar molecules incorporating a 4,7-diphenyl-2,1,3-benzothiadiazole core

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Abstract: A new polycatenar liquid crystal **I** containing a 4,7-diphenyl-2,1,3-benzothiadiazole core and three alkoxy chains at each end has been synthesized *via* copper catalyzed azide-alkyne click reaction and investigated by polarizing microscopy, DSC, XRD scattering, SEM, UV-vis spectroscopy and photoluminescence measurements. This compound can self-assemble into an oblique columnar liquid crystalline phase in the bulk state and form organogels in different organic solvents. It shows highly fluorescent emission with large Stokes shift in solution and has binding selectivity to Li⁺ among a series of cations in DMSO-CH₂Cl₂ solution.

Key words: benzothiadiazole; columnar liquid crystal; organogel; fluorescent chemosensor; azide-alkyne click reaction

1. Introduction

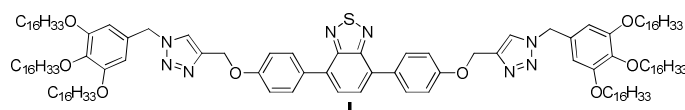
Design of low-molecular-weight linear π -conjugated molecules which can self-organize into ordered nanostructures with potential nanotechnological application is of current interest.¹ Liquid crystals (LCs)² represent soft self-assembled materials with significant technological importance^{2,3}

and provide routes to increase complexity in soft self-assembly.⁴ Physical gels with fibrous aggregates formed by one-dimensional (1D) self-assembly of molecules in solvents have also attracted a great deal of attention not only as an interesting mode of self-assembly, but also for various potential application such as photovoltaics,^{5,6} templating,⁷ controlled drug release,⁸ energy transfer⁹ and others. Molecules that can exhibit both, liquid crystalline and gelation properties, have recently been reported.¹⁰

Benzothiadiazole (BTD) derived molecules are widely investigated nowadays due to their well known photophysical properties such as high extinction coefficient, intense fluorescence,¹¹ and large Stokes shift,¹² with potential as optical materials and chemosensors.¹³⁻¹⁸ BTD derivatives are now also widely employed as semiconducting materials such as field-effect transistors (FETs) because of their high electron affinity.¹⁹ There are previous reports about LCs containing BTD units and most of them showed smectic and nematic phases,²⁰⁻²⁷ but only few polycatenar BTD derivatives with columnar phases have been reported so far.^{28,29} In some cases, liquid crystalline BTD derivatives with SmC or nematic phases gave macroscopically ordered films with good charge-transport properties, exhibiting good carrier mobilities which is a favorable morphology for FET applications with improved performance.^{25,30}

Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC)³¹ represents one of the most efficient approaches for interconnecting smaller units to larger entities, especially for chemical transformation to create new fluorescent molecules with desirable properties. The resulting triazole ring could represent a π -conjugated core structure providing desirable materials properties.³² Few reports about application of the CuAAC reaction for the synthesis of rod-like,³³ disc-like, star shaped³⁴ and bent-core³⁵ LCs have appeared quite recently. Materials with nematic, SmA, SmC and columnar phases and in one case a bicontinuous cubic phase^{34d} have been obtained by this approach. We have recently reported the first use of this synthetic method for the synthesis of polyphilic molecules forming spheroidal cubic phases with micellar and monolayer vesicular structures.³⁶ Chemosensors containing 2,1,3-benzothiadiazole and triazole units have been recently reported and in all cases, the 1,2,3-triazole rings were anchored directly to the BTD units.^{32,37}

Herein we employed the click reaction for the construction of hexacatenar mesogens incorporating a 4,7-diphenyl-2,1,3-benzothiadiazole (DBTD) core and three alkoxy chains at each terminus (Fig. 1). This compound has both, liquid crystallinity and gelation properties, and it can be used as fluorescence chemosensor for selective response to different metal ions in solution and therefore it can be considered as a multifunctional material.



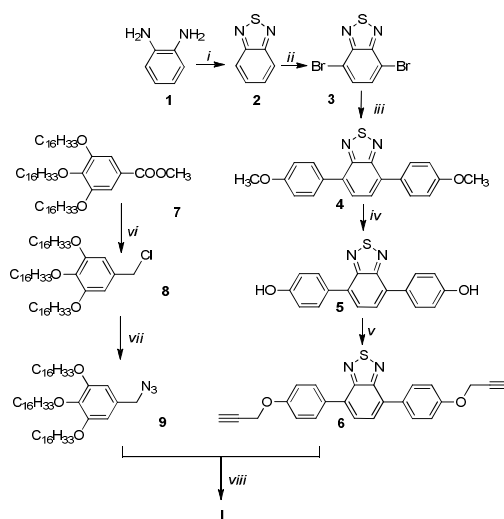
Heating: Cr 59 °C [88.8 kJ mol⁻¹] Col_{ob} 105 °C [13.1 kJ mol⁻¹] Iso
Cooling: Iso 101 °C [11.9 kJ mol⁻¹] Col_{ob} 46 °C [100.9 kJ mol⁻¹] Cr

Fig. 1. Structure of compound **I** with transition temperatures ($T/^\circ\text{C}$) and associated enthalpy values as determined by DSC (peak temperatures, 5 K min⁻¹); abbreviation: Cr = crystalline solid; Col_{ob} = oblique columnar LC phase; Iso = isotropic liquid state.

2. Results and discussion

2.1 Synthesis

The target compound **I** was prepared by the CuAAC reaction between bispropargylether **6** and benzyl azide **9** as shown in Scheme 1. The benzyl azide **9** was obtained by the nucleophilic substitution of benzyl chloride **8** with sodium azide.³⁶ Commercially available *o*-phenylenediamine **1** was treated with freshly distilled thionyl chloride in the presence of triethylamine in CH₂Cl₂, affording 2,1,3-benzothiadiazole **2**,³⁸ which was dibrominated with Br₂/HBr.^{38f-g} The obtained 4,7-dibromo-2,1,3-benzothiadiazole **3** was coupled with two equivalents of 4-methoxy-phenylboronic acid under standard Suzuki conditions with Pd(PPh₃)₄^{39,40} and afforded the 4,7-bis(4-methoxyphenyl)-2,1,3-benzothiadiazole **4**.¹¹ Demethylation of **4** using HBr (33% in HOAc) yielded compound **5**,³⁹ which was etherified with propargyl bromide to give the bispropargylether **6**.³⁹ Compound **6** was used for CuAAC reaction^{36a} with the benzyl azide **9** to yield the target product **I** which was purified by column chromatography. The detailed synthetic procedures and analytical data are given in the Supporting Information.

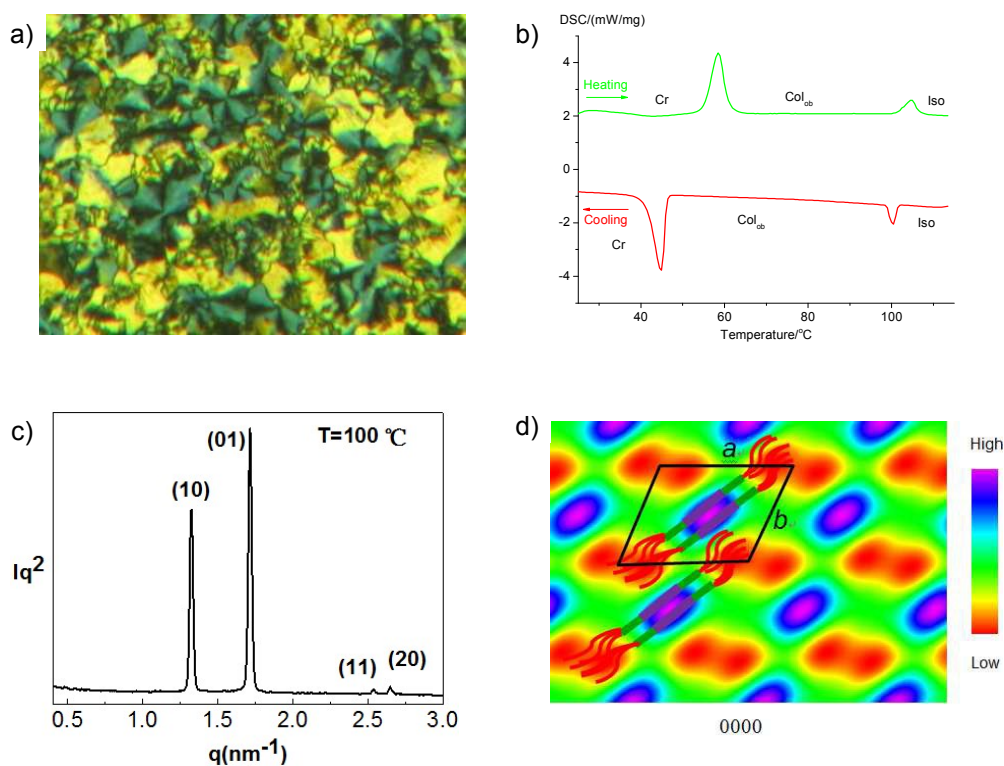


Scheme 1. Synthesis of compound **I**. Reagents and conditions: (i) SOCl₂, Et₃N, CH₂Cl₂, 93%; (ii) Br₂, HBr, 95%; (iii) 4-methoxyphenyl boronic acid, Pd(PPh₃)₄, Cs₂CO₃, KF, H₂O, reflux, 12 h, 60%; (iv) Bu₄NBr, HBr (33% in HOAc), 80%; (v) K₂CO₃, KI, propargyl bromide, 80 °C, CH₃CN, 12 h, 94%; (vi) a) LiAlH₄, THF, 96%; b) SOCl₂, THF, 93%; (vii) NaN₃, KI, DMF, 97%; (viii) CuSO₄·5H₂O, Sodium ascorbate, TBA : H₂O = 1 : 1, THF, 61%.

2.2 Mesomorphic properties

The LC self-assembly of compound **I** was investigated by polarized optical microscopy (POM, Fig. 2a), differential scanning calorimetry (DSC, Fig. 2b), and X-ray diffraction (XRD, Fig. 2c). The thermotropic phase sequence and the transition temperatures are shown in Fig. 1. The texture of the LC phase observed by POM between crossed polarizers is characterized by spherulitic domains as typical for columnar phases (Fig. 2a). Shearing the sample leads to flow which removes this texture, this confirms the LC state of the material. The SAXS pattern of **I** at 100 °C shows two strong and two weak reflections (Fig. 2c). The small angle reflections were indexed as (10), (01), (11) and (20) reflections of an oblique lattice⁴¹ with $a = 5.1$ nm, $b = 4.0$ nm and $\gamma = 67^\circ$ ($T = 100$ °C). The

electron density map reconstructed from the powder pattern (Fig. 2d; for alternative phase combinations, see Fig. S1 in the Supporting Information) shows high electron density areas (blue, purple) involving the DBTD cores, which are surrounded by a medium electron density continuum (green) involving the benzylether groups, triazoles and some of the alkyl chains. The majority of the alkyl chains form the low electron density areas (red), supporting the proposed organization of the molecules in this mesophase (Fig. 2d-f). The number of molecules located within a hypothetical unit cell with a height of 0.45 nm (n_{cell}) has been calculated to be approximately two ($n_{\text{cell}} = 2.3$) by dividing the unit cell volume ($V_{\text{cell}} = 8.44 \text{ nm}^3$) by the molecular volume (calculated using Imirzis increments,⁴² $V_{\text{mol}} = 3.24 \text{ nm}^3$) and assuming a packing coefficient being the average between the crystalline ($k = 0.7^{43}$) and the liquid state ($k = 0.55$). Thus, the molecules are organized in ribbons formed by on average two molecules arranged side-by-side in their cross section. The fixation of the three alkyl chains at each end leads to a staggering of these ribbons to optimize the space filling, thus providing the oblique 2D lattice. The long diagonal of the oblique lattice is 7.5 nm, which agrees well with the molecular length in the stretched conformation ($L_{\text{mol}} = 7.6 \text{ nm}$, see Fig 2e). Therefore, in agreement with the electron density map, the molecules are not arranged parallel to a or b but nearly parallel to the longer diagonal.



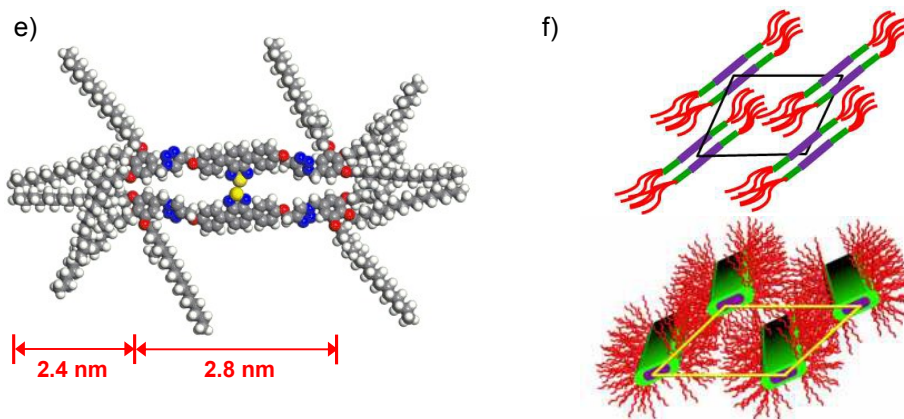


Fig. 2. LC phases of compound **I**: a) Texture of the Col_{ob} phase as seen between crossed polarizers at $T = 90$ °C; b) DSC heating and cooling scans (5 K min^{-1} , second scans); c) SAXS diffractogram at $T = 100$ °C; d) electron density map as reconstructed from the diffraction pattern in c), for the color code, see bar on the right, e) model showing the organization of two molecules in the cross section through a single column; f) models for the molecular arrangement in Col_{ob} phase.

2.3 Gelation properties

The gelation ability of compound **I** was tested in various organic solvents at a concentration of 3.0 mg/mL and the results are summarized in Table 1. **I** has the ability to gel in DMF, *n*-butanol, and partially in cyclohexane and *n*-hexane, but it precipitates in ethyl acetate, acetone and 1,4-dioxane. A yellow gel can be obtained by cooling the heated solution of **I** in *n*-butanol quickly below 20 °C or slowly down to room temperature. The yellow gel shows green fluorescence under irradiation with 365 nm light (Fig. 3a, b). The sol-gel transition temperature is 60 °C (Fig. 3c). The morphology of the gel was investigated by scanning electron microscopy (SEM). The SEM image of the xerogel formed by **I** (Fig. 4a, b) shows the formation of three-dimensional networks composed of entangled fibrous aggregates. The approximate diameter of the fibers is 145-250 nm. The length is more than 20 μm . On the basis of this result, it is assumed that compound **I** forms fibrous aggregates in the solvents.

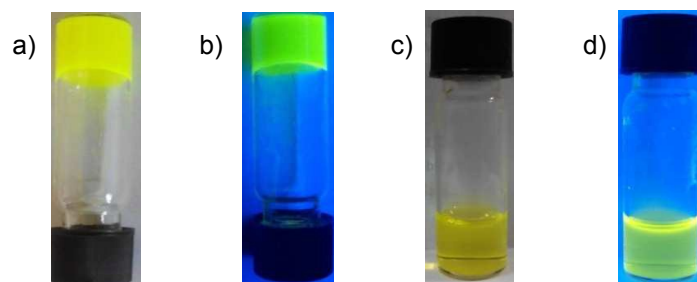


Fig. 3. Photograph of gels prepared with **I** in *n*-butanol, a,b) at $T = 20$ °C, a) without irradiation; b) under irradiation with 365 nm light; c,d) heated to 65 °C, c) without irradiation and d) under irradiation with 365 nm light.

Table 1. Gelation properties of **I**^a

Solvent	I	Solvent	I
Chloroform	S	1,4-Dioxane	P
Ethyl acetate	P	Cyclohexane	PG
THF	S	Hexane	PG
Methanol	IS	<i>n</i> -Butanol	G
Acetone	P	Toluene	S
DMF	G		

^a S = solution, P = precipitation, G = gelation, PG = partial gelation, IS = insoluble gelator concentration is 3.0 mg/mL; gels formed at room temperature.

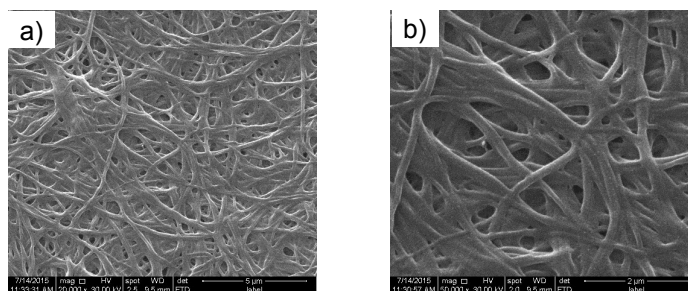


Fig. 4. Selected SEM images of xerogel formed by **I** in *n*-butanol: a) scale bar is 5 μm; b) scale bar is 2 μm.

2.4 Absorption and emission properties

The UV-vis absorption and fluorescence spectroscopic data in CH₂Cl₂ (DCM) solution ($c = 10^{-6}$ mol L⁻¹) and in the solid state of compound **I** are shown in Fig. 5. This compound shows the maximum absorption peak at 403 nm in DCM solution which may be attributed to the π - π^* transition. The red shift (of about 7 nm in the solid state) suggests the formation of π -stacked aggregates with a *J*-type parallel stacking mode in the solid state.⁴⁴ The photoluminescence (PL) spectrum in the solid state exhibits a blue shifted emission with maxima at 523 nm, while the solution displays a structured emission with a maximum at 535 nm. Hence the Stokes shift has a remarkably large value of 132 and 113 nm in DCM solution and in the solid state respectively. Compound **4** (Scheme 1) with methoxy groups replacing the triazole and trialkoxybenzene units has the maximum absorption peak at 409 nm and maximum emission at 542 nm (DCM, $c = 10^{-6}$ mol L⁻¹), respectively.¹¹ Both, the absorption maxima and the emission peaks of compounds **I** and **4** are very similar, indicating that for both compounds the DBTD core acts as chromophore and that the triazole rings and the trialkoxybenzyl units in compound **I** do not contribute to π conjugation of the DBTD core.

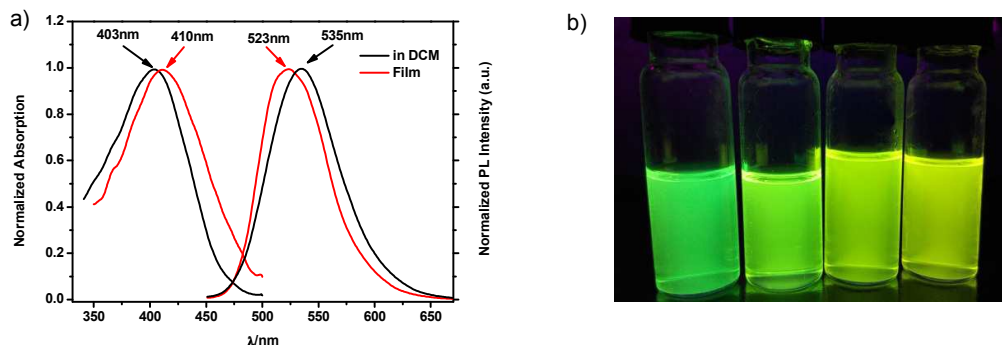


Fig. 5. a) Normalized spectra and emission spectra of **I** (10^{-6} M) at 20 °C; b) Fluorescence images of **I** in hexane, toluene, THF, and DCM (from left to right).

The energy band gap of compound **I**, which was estimated from the onset of the absorption in thin film, is about 2.67 eV.⁴⁵ The HOMO and LUMO energy levels of **I** in thin films were determined by cyclic voltammetry on a glassy carbon electrode (Fig. S3 and Table S2 in the Supporting Information) from the onset of oxidative or reductive potentials and the band gap is calculated to be 2.44 eV. Consequently, the band-gap was almost in agreement with those obtained from their absorption spectra in thin films. In order to investigate the conformation and electron distributions of **I**, calculations based on density functional theory (DFT) with the Gaussian 03W program package at B3LYP/(6-31G, d) level were performed with the model compound **I**, having methoxy groups instead of the $\text{OC}_{16}\text{H}_{33}$ chains. The electron distributions of the HOMO and LUMO of **I** are shown in Fig. 6. In the minimum energy conformation compound **I** adopts almost a boat shaped conformation with kinks provided by the CH_2 groups, linking the peripheral phenyl groups to the triazoles. As it can be seen in the HOMO orbital, the electrons are localized on the phenyl rings and the benzothiadiazole unit of the central π -conjugated DBTD core, in the LUMO orbital, the electrons are mainly localized on the benzothiadiazole unit, resuming that intramolecular charge transfer (ICT) exists in the **I** molecules.

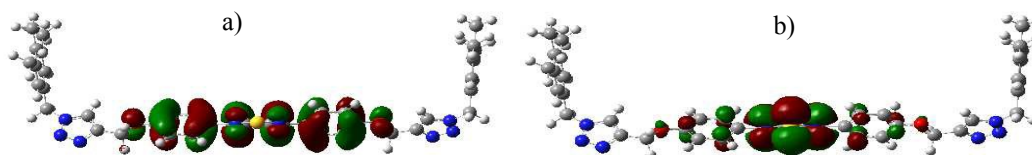


Fig. 6. a) HOMO orbital; b) LUMO orbital of **I**/1 (calculated using the DFT/B3LYP, 6-31G, d functional).

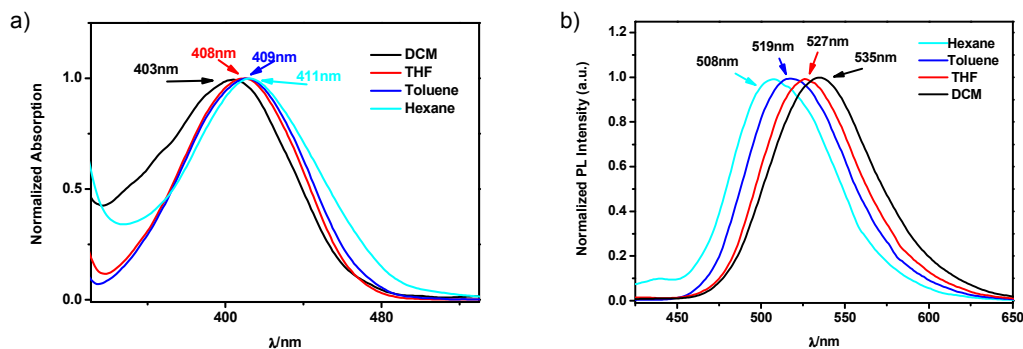


Fig. 7. a) UV-vis spectra of **I** (10^{-6} M) at 20 °C in hexane, toluene, THF, DCM; b) Fluorescence spectra of **I** in hexane, toluene, THF, DCM excited at 412 nm, 409 nm, 408 nm, 403 nm respectively.

Table 2 Fluorescence and excitation data of **I** (10^{-6} M) at 20°C, where λ_{exc} is the excitation maximum, λ_{em} is the fluorescence emission maximum, and $\Delta\lambda_{\text{ST}}$ is the Stokes shift^a

Compd.	Solvent	λ_{exc}	λ_{em}	$\Delta\lambda_{\text{ST}}$	Φ_{FL}
I	DCM	403 nm	535 nm	132 nm	0.50
	Chloroform	407 nm	539 nm	132 nm	0.55
	THF	408 nm	527 nm	119 nm	0.61
	Toluene	409 nm	519 nm	110nm	0.58
	Hexane	411nm	508 nm	97 nm	0.53
	film	410 nm	523 nm	113 nm	- ^b

^a The Stokes shift was obtained from the difference of the emission and absorption maximum ($\Delta\lambda_{\text{ST}} = \lambda_{\text{em}} - \lambda_{\text{exc}}$); ^b not measured.

For further investigation of the influence of solvent polarity on the optical properties of the benzothiadiazole derivative **I**, the UV-vis and fluorescence spectra were measured in various solvents (see Fig. 7 and Table 2). The maxima of the absorption peaks are only slightly red shifted with increasing solvent polarity and the emission bands are shifted to longer wavelengths with an increase in the solvent polarity, from 508 nm (hexane) to 519 nm (toluene) to 527 nm (THF).⁴⁶ Furthermore, fluorescence quantum yields (Φ_{FL}) of compound **I** in the above solvents were determined relative to quinine sulfate in sulfuric acid aqueous solution and calculated according to the literature (see Table 2).⁴⁷ The highest Φ_{FL} value (0.61) is achieved in the polar solvent THF. It seems that the polar solvent media causes a disturbance of the solvation quenching because in the polarized excited state, the positive charge may be delocalized among the donor moieties⁴⁸ Compared to the methoxy substituted compound **4** ($\Phi_{\text{FL}} = 0.78$ in DCM), the Φ_{FL} value of the new compound **I** ($\Phi_{\text{FL}} = 0.50$ in DCM) is slightly lower, but it still keeps a high quantum yield.

2.5 Chemosensor behavior

To get insights into the binding properties of compound **I** toward metal ions, the fluorescence profiles of **I** in the presence of 30 equiv of selected cations in different solutions were investigated. In the solution of $\text{CH}_3\text{CN} : \text{DCM} = 2 : 1$ (Fig. 8c,d), the fluorescence emission was significantly

quenched by Cu^{2+} , as already observed in some triazole containing compounds.⁴⁹ The fluorescence quenching decreases in the sequence Cu^{2+} , Ca^{2+} , Ba^{2+} , Co^{2+} , Na^+ , Mg^{2+} , Cr^{3+} , Cd^{2+} , Zn^{2+} , Li^+ , Ni^{2+} , Ag^+ , K^+ (Fig. 8c,d). However in the solution of DMSO : DCM = 2 : 1, the fluorescence emission was significantly quenched by Li^+ , in this case the sequence is very different and the fluorescence quenching decreases in the sequence Li^+ , Ag^+ , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , Cr^{3+} , Al^{3+} , Pb^{2+} , Ni^{2+} , Ca^{2+} , Mg^{2+} , Ba^{2+} from high to low (Fig. 8a,b). Therefore, the selectivity of compound **I** toward different metal ions could be varied depending on the type of solvents, namely the binding selectivity among a series of cations could be controlled by changing the type of solvent. The result also shows an interesting finding that for charge dense ions, such as Mg^{2+} , Ca^{2+} and Ba^{2+} in $\text{CH}_3\text{CN} : \text{DCM} = 2 : 1$, the binding selectivity is ranked in the top region, but in $\text{DMSO} : \text{DCM} = 2 : 1$, the binding selectivity of these charge dense ions is the lowest. The possible reason is that DMSO can provide additional hydrogen bonding with the binding sites in the structure of compound **I** (the triazole unit) while CH_3CN as solvent does not,³⁷ this may make the difference in selectivity among the series of cations in different solvents. Compared with the previously reported BTD derivatives, in which triazoles were anchored directly on the BTD core,^{32c,k,1,37} the highest cation selective fluorescence quenching efficiency of compound **I** (53.6 %) is slightly weaker than those of the reported BTD derivatives (almost 73 %).

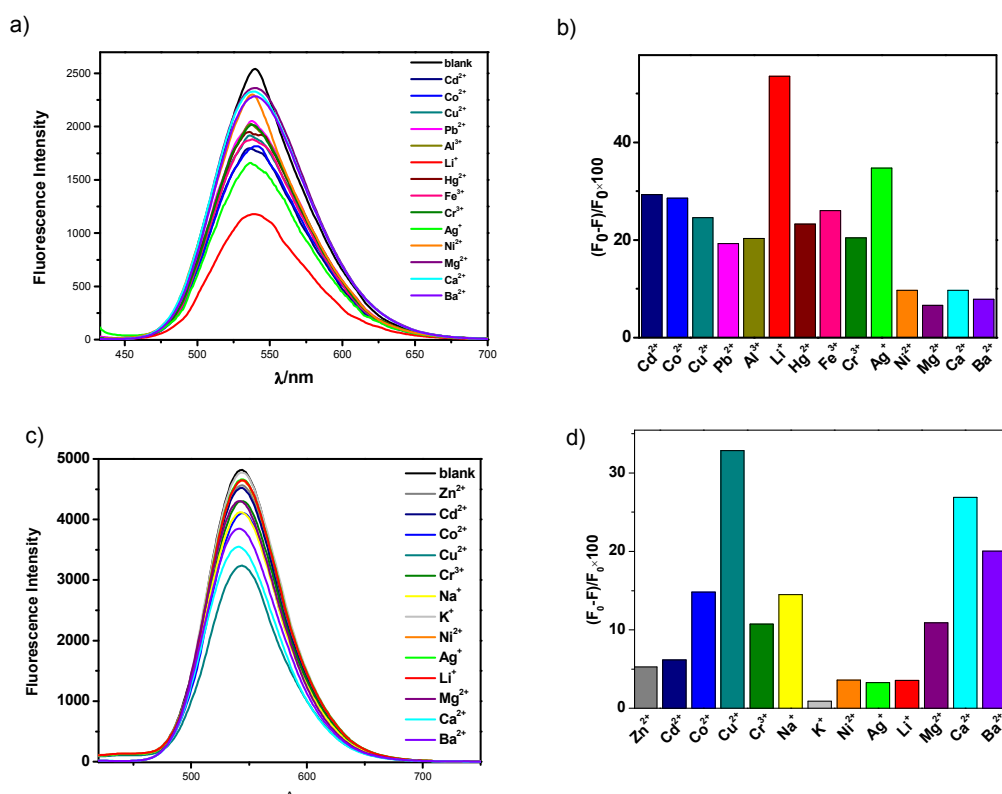


Fig. 8. Fluorescence spectra of compound **I** (10^{-6} M) at room temperature upon addition of various metal cations (30 equiv, except for K^+ , Ca^{2+} , Ba^{2+} and Mg^{2+} the counter anion are Cl^- for other cations, the counter anions are ClO_4^-): a,b) in DMSO : DCM = 2 : 1 ($\lambda_{\text{ex}} = 423$ nm) and c,d) in MeCN: CH_2Cl_2 (2:1) (V/V) ($\lambda_{\text{ex}} = 398$ nm); $(F_0 - F)/F_0 \times 100$ depicts the cation selective fluorescence quenching efficiency of compound **I** namely the fluorescence responses of different metal ions; abbreviation: F_0 = the fluorescence emission maximum of blank sample; F = the fluorescence the fluorescence emission maximum of samples with addition of different metal ions.

For the selective response of **I** to Li^+ , spectral titration was performed in solution of DMSO : DCM = 2 : 1; with the addition of Li^+ (from 0.5 to 30 equiv), the emission peak at 542 nm decreased gradually and finally reached its fluorescence quenching plateau at ~ 9 equiv (Fig. 9).^{32c,50} Although the triazoles are not in conjugation with the 4,7-diphenyl-3,2,1-benzothiadiazole unit (CH_2 group interrupts the conjugation), compound **I** can still have long excitation and emission wavelength while keeping a high fluorescence quantum yield. Therefore, compound **I** could be used as chemosensor exhibiting strong and selective binding to Li^+ in the solution of DMSO : DCM = 2 : 1.

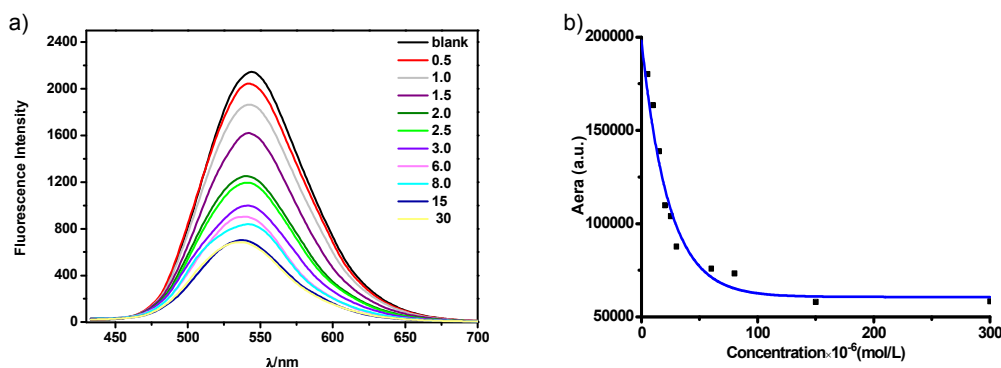


Fig. 9. a, b) Fluorescence spectra of compound **I** (3.33×10^{-6} M) at 20 °C upon addition of Li^+ (from 0.50 to 27 equiv) in DMSO : DCM = 2 : 1 ($\lambda_{\text{ex}} = 423$ nm).

3. Conclusion

A new fluorescent polycatenar liquid crystal **I** containing a 4,7-diphenyl-2,1,3-benzothiadiazole core and three alkoxy chains at each terminal was designed and synthesized. This compound can self-assemble into a liquid crystalline oblique columnar phase in its pure state and forms fluorescent organogels in different organic solvents. At the same time, it shows intense fluorescent emission with large Stokes shift in solution and has good binding selectivity to Li^+ among a series of cations in DMSO-DCM solution. Compared with the reported BTB derivatives in which triazoles were anchored directly on the BTB core,^{32c,k,1,37} the presence of the methylene units between BTB and the triazole rings in this compound does not have a negative impact on the photo-electronic properties and this compound still has a high fluorescence quantum yield ($\Phi_F = 0.61$ in THF) and a good selectivity to Li^+ . Thus, this fluorescent compound with low energy band gap, forming a columnar mesophase structure in the pure state and organogels in solution, could form macroscopically ordered films both in the pure state and from solution in organic solvents. This is favorable for FET applications as well as for low-cost deposition or solution-processing techniques for large-area organic electronics applications.²⁷

Acknowledgements

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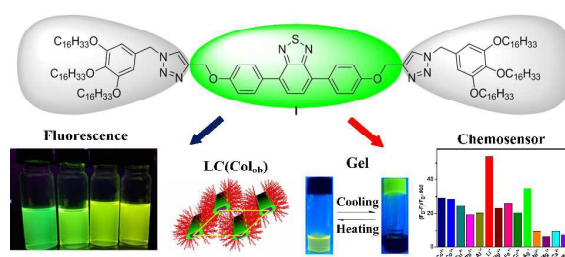
Synthesis and self-assembly of luminescent hexacatenar molecules incorporating a 4,7-diphenyl-2,1,3-benzothiadiazole core

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A luminescent hexacatenar molecule forms an oblique columnar liquid crystal, gels in various organic solvents, and has binding selectivity to Li⁺ in DMSO-CH₂Cl₂ solution.