Supramolecular self-assembly carbazolyl radicals nanospheres triggered by ultraviolet light for explosives sensing

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Abstract: In this work, we designed and synthesized a carbazole-type molecule that can form carbazolyl radicals in chloroform solution under the irradiation of UV light. The process is accompanied by an obvious change in the emission color from blue to bright green. The radicals and the neutral molecules assemble together and form nanospheres through synergistic effect of π - π stacking, intermolecular hydrogen bonds and charge transfer interaction. High resolution-transmission electron microscopy (HR-TEM) is used to confirm the nanospheres. The radius sizes of the nanospheres are mainly in 80~100 nm. Further, these nanospheres act as the fluorescence sensor for explosives detection, and they exhibit high selectivity and sensitivity to 2, 4, 6-trinitrophenol (TNP). The limit of detection for nanospheres is 1.2×10^{-7} M.

1. Introduction

Supramolecular self-assembly based on small organic molecules is of particular interest for various domains of application.[1] Among them, light-responsive functional materials have drawn more attention owing to their excellent electrical and optical properties, easy processability and flexibility.[2] The applications of these materials include photodetectors,[3] optically switchable electronic devices,[4] photocatalysis[5] and light-induced gene expression.[6] Therefore, the development of functional nanomaterials supported by the response to light is fundamentally important to extensive research interest and technical demand in material science.

Recently, Nicolas Giuseppone et al. reported triarylamine-type molecules could produce triarylammonium radicals in chloroform (CHCl_3) after they were exposed to white light. Then large fibrillar 3D aggregates were formed. These aggregates as nanowires exhibited the metallic behavior.[7] Ling Zang et al. reported the fluorescence emission of imidazole in halogenated solvents can be quenched by γ radiation, which was used to detect the γ radiation.[8] Paolo Samorì et al. reported an amphiphilic D-A π -conjugated dyad could form ordered nanoribbons

after being exposed to white light. These nanoribbons were used as the ultrafast and ultrasensitive humidity sensor.[9]

Fluorescence detection to explosives has attracted great attention because it has the advantages of low cost, high sensitivity and portability.[10,11] In particular, 2, 4, 6-trinitrophenol (TNP) is one of the most dangerous explosives, and is also toxic to environment and human health.[12] Moreover, the discrimination between TNP and TNT (2, 4, 6-Trinitrotoluene) is still a serious challenge due to their similarly deficient groups.[13] So Looking for the TNP detector with high selectivity and sensitivity is highly demanded.

Herein, we reported a carbazole-type molecule, OcCz-PAc, which could generate nanospheres in CHCl_3 through supramolecular self-assemble under the irradiation of UV light. The nanospheres solution is more sensitive to TNP than to other explosives with the limit of detection of 1.2×10^{-7} M. The main reason causing the remarkable fluorescence quenching of OcCz-PAc nanospheres could be attributed to the formation of no-fluorescence complexes.

2. Experimental

2.1 Chemicals and measurement

All reagents, unless otherwise specified, were obtained from Aldrich, Acros and TCI Chemical Co. and used as received. All the solvents were dried and purified by distillation. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry nitrogen. Column chromatography was performed using silica gel (200-300 mesh). The ^1H NMR and ^{13}C NMR were recorded on a Bruker AVANCZ 500 spectrometer at 500 MHz, using deuterated chloroform (CDCl_3) as the solvent at 298 K, and tetramethylsilane (TMS) as the internal standard. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a model UV-3100 spectrophotometer. Fluorescence spectra were performed using a model RF-5301PC spectrophotometer. Dynamic Light Scattering spectra (DLS) were obtained by ALV-CGS-3. The HR-TEM experiment was performed using a JEOL model JEM-3010 with an acceleration voltage of 300 kV.

2.2 Synthesis

3, 6-dibromo-9H-carbazole:

Carbazole (1, 30.1 mM, 5 g) and N-bromosuccinimide (2.3, 69.21 mM, 12.32 g) were dissolved in CHCl_3 (200 mL), the reaction mixture stirred in dark for 24 h at room temperature.

Subsequently, the solution was poured into water (100 mL) and extracted with dichloromethane (CH_2Cl_2), the crude products were recrystallized from methanol as white powder in 75 % yield. δ H (500 MHz, DMSO) 11.59 (1 H, s), 8.43 (2 H, s), 7.72-7.30 (4 H, m). MALDI-TOF-MS: 324.83.

3, 6-bis(octyloxy)-9H-carbazole(OcCz):

Sodium (8.86, 109 mM, 2.5 g) was dissolved in octanol (80 mL) at room temperature. The mixture of 3, 6-dibromo-9H-carbazole (1, 12.3 mM, 4 g) and copper(I) iodide (2.1, 25.79 mM, 4.9 g) was dissolved in N, N-dimethylformamide (DMF) (8 mL) and mixed with the octanol solution stirred at 140 °C for 36 h in a nitrogen atmosphere. The solution was cooled down to room temperature, filtered and the solvent was evaporated under reduced pressure. The crude products were purified using a silica gel column (CH_2Cl_2 /petroleum ether 2:1) to afford a white powder in 55 % yield. δ H (500 MHz, DMSO) 10.77 (1 H, s), 7.66 (2 H, d, $J=2.4$), 7.31 (2 H, d, $J=8.7$), 6.97 (2 H, dd, $J=8.7$), 4.03 (4 H, t, $J=6.5$), 1.85-1.68 (4 H, m), 1.54-1.41 (4 H, m), 1.39-1.21 (17 H, m), 0.88 (6 H, t, $J=6.8$). MALDI-TOF-MS: 423.29.

9-(4-nitrophenyl)-3, 6-bis(octyloxy)-9H-carbazole:

3, 6-bis(octyloxy)-9H-carbazole (1, 0.83 mM, 350 mg), 1-bromo-4-nitrobenzene (4, 3.3 mM, 667.6 mg), potassium carbonate (4, 4.15 mM, 573 mg), copper(I) iodide (0.1, 0.083 mM, 15.7 mg) were dissolved in DMF (5 mL). The solution stirred at 150 °C for 36 h in a nitrogen atmosphere. The solution was cooled down to room temperature. The crude products were purified using a silica gel column (CH_2Cl_2 /petroleum ether 1:1) to afford a yellow powder in 55 % yield. δ H (500 MHz, CDCl_3) 8.48 (2 H, d, $J=9.0$), 7.79 (2 H, d, $J=9.0$), 7.54 (2 H, t, $J=16.1$), 7.45 (2 H, d, $J=8.9$), 7.08 (2 H, dd, $J=8.9$), 4.21-4.01 (4 H, m), 1.96-1.78 (4 H, m), 1.39-1.20 (18 H, m), 0.94 (9 H, dd, $J=22.8$). MALDI-TOF-MS: 544.01.

N-(4-(3, 6-bis(octyloxy)-9H-carbazol-9-yl)phenyl)acetamide (OcCz-PAc):

A mixture of 9-(4-nitrophenyl)-3, 6-bis(octyloxy)-9H-carbazole (1, 0.59 mM, 320 mg) and palladium on charcoal (0.1, 0.08 mM, 8.496 mg) was in ethanol (10 mL). Hydrazine (3.7, 2.18 mM, 110.308 mg) was then added dropwise to solution and stirred for 12 h at 60 °C. The organic phase was evaporated under reduced pressure and the resulting product N-(4-(3, 6-bis(octyloxy)-9H-carbazol-9-yl)aniline was clean enough to be used in the next step. A solution of N-(4-(3, 6-bis(octyloxy)-9H-carbazol-9-yl)aniline (1, 0.55 mM, 283 mg), triethylamine (1.1, 0.605, 61.22 mg) was in CH_2Cl_2 (10 mL). The cooled solution of chloroacetylchloride (1.1, 0.605, 47.49 mg) was added dropwise to mixture solution at 0 °C. The solution was stirred for 12 h at room

temperature. Further, the crude mixture was purified using a silica gel column (ethyl acetate/petroleum ether 1: 4) to afford a white powder in 45 % yield over 2 steps. δ H (500 MHz, DMSO) 10.19 (1 H, s), 7.84 (2 H, d, $J=8.8$), 7.80 (2 H, d, $J=2.5$), 7.49 (2 H, d, $J=8.8$), 7.24 (2 H, d, $J=8.9$), 7.01 (2 H, dd, $J=8.9$), 4.07 (4 H, t, $J=6.5$), 2.11 (3 H, s), 1.85-1.70 (4 H, m), 1.53-1.41 (4 H, m), 1.40-1.22 (16 H, m), 0.88 (6 H, t, $J=6.9$). δ C (126 MHz, DMSO) 168.90 (s), 153.42 (s), 136.00 (s), 127.03 (s), 123.59 (s), 120.69 (s), 116.13 (s), 110.79 (s), 104.76 (s), 68.65 (s), 31.74 (s), 29.49- 29.09 (m), 26.11 (s), 22.58 (s), 14.43 (s). MALDI-TOF-MS: 556.67. Calcd. for $C_{36}H_{48}N_2O_3$: C: 77.66, H: 8.69, N: 5.03. Found: C: 77.95, H: 8.63, N: 4.98.

2.3 Fluorescence detection of TNP and other explosives

The fresh solution of OcCz-PAC in $CHCl_3$ (10 μ M) was exposed to UV light (365 nm) for 600 s. Then the $CHCl_3$ solvent was evaporated under reduced pressure. The left solid was re-dissolved in THF with a concentration of 2 μ M. Accordingly, 3 mL solution were put into the quartz cuvette, then adding 3 μ L TNP (0.01 M) into the cuvette and stirring for 10 s, and the fluorescence spectrum was recorded under the excitation at 340 nm. The TNP concentration response PL characterization of nanospheres was carried out according to similar process.

3. Results and discussion

The synthetic routes of OcCz-PAC monomer are shown in Scheme 1. The precursor OcCz is synthesized through Williamson reaction, carbazole is modified with octyloxy to increase the solubility. Subsequently, the OcCz-PAC is synthesized with amide group, which is of importance to stabilize the self-assembled aggregates by intermolecular hydrogen bonds.

InsertScheme 1

1H NMR is a key technology to illustrate the formation of carbazolyl radicals.[14, 15] OcCz-PAC is then investigated by 1H NMR in $CDCl_3$ (Figure 1). Figure 1a illustrates the 1H NMR spectrum of the fresh solution of OcCz-PAC in $CDCl_3$ corresponding to the pure product. After the solution of OcCz-PAC is exposed to UV light (365 nm) for 600 s (Figure 1b), the signals of the aromatic protons remarkably decrease and the fine structures of other protons signals became broader. Importantly, the phenomenon can only be observed in chlorinated solvent. This suggests that OcCz-PAC could transfer one electron to chlorinated solvent resulting in the formation of carbazolyl radical cations under the irradiation of UV light, which is similar to the formation of triarylammonium radicals in $CHCl_3$. [7, 16]

Insert Figure 1

Some aggregates are created after the CHCl_3 solution of OcCz-PAC is exposed to UV light. Dynamic light scattering (DLS) is employed to investigate the aggregates of OcCz-PAC. As shown in Figure 2a, the main size of the aggregates peaks at 100 nm in hydrodynamic radius after the exposure of OcCz-PAC solution to UV light for 600 s. At the same time, there are a few larger aggregates with the diameter of micrometers. High resolution-transmission electron microscopy (HR-TEM) is used to explore the structure of these aggregates. As can be seen in Figure 2b, there are a large number of nanospheres distributed on the copper net. The radius sizes of the nanospheres are mainly in 80~100 nm, which agree with the result of DLS. The mechanism of the formation of nanospheres is attributed to that the carbazolyl radical cations induced the molecular assembly between the carbazolyl radical cations and the neutral molecules through synergistic effect of π - π stacking and charge transfer interactions.[17] Moreover, amide group is of importance to stabilize the self-assembled aggregates by intermolecular hydrogen bonds.

Insert Figure 2

The PL spectra of OcCz-PAC in CHCl_3 as a function of the irradiating time are recorded. As shown in Figure 3a, the fresh OcCz-PAC solution has a blue emission peaking at 391 nm. After the exposure to UV light (365 nm) for 120 s, the blue emission is gradually quenched. Meanwhile, a new fluorescence band emerges peaking at 494 nm, which indicates an aggregation process of self-assembly. The fresh OcCz-PAC solution is colorless and the irradiated solution is pale orange as shown in inset I of Figure 3b. The irradiated solution excited by the UV light at 365 nm displays a bright green emission as shown in inset II of Figure 3b. Interestingly, these nanospheres are stable in various solvents, such as THF, CH_2Cl_2 , CHCl_3 and DMF, which enable them as the explosives sensors in different solvents.

Insert Figure 3

Then the OcCz-PAC nanospheres are used as the TNP detector. As shown in Figure 4a, the fluorescence intensity of OcCz-PAC nanospheres in THF obviously decline upon the gradual addition of TNP from 0 to 1×10^{-4} M. The fluorescent static quenching coefficient K_{sv} is an important parameter to evaluate the sensor, and can be calculated according to Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{sv}[Q]$$

where I_0 is the maximum fluorescence intensity of OcCz-PAC nanospheres solution and I is the intensity of OcCz-PAC nanospheres solution after adding TNP solution, Q is the TNP concentration. The K_{sv} is calculated to be $2.66 \times 10^4 \text{ M}^{-1}$. Figure 4b shows the changes of the fluorescence intensity of OcCz-PAC nanospheres solution as a function of the concentration of TNP solution.

Insert Figure 4

According to the limit of detection (LOD) $= 3\sigma/m$, [18] where σ is the standard deviation of blank measurements and m is the slope of change of intensity versus sample concentration, the LOD for TNP is calculated to be $1.2 \times 10^{-7} \text{ M}$, which is comparable to the reported materials. Some reported LODs of different materials to detect TNP solution have been summarized in Table 1.

Insert Table 1

The solution of OcCz-PAC nanospheres exhibit not only high sensitivity to TNP solution but also high selectivity. As we can see from Figure 5a, some common explosives are also tested, including 2, 4, 6-Trinitrotoluene (TNT), Pentaerythritol tetranitrate (PETN), 2, 4, 6-Trinitrophenylmethylnitramine (Tetryl), 2, 4-Dinitrotoluene (DNT) and 1, 3, 5-Trinitro-1, 3, 5-triazacyclohexane (RDX). The results indicate the solution of OcCz-PAC nanospheres is of far better selectivity to TNP than to other explosives.

So far, the fluorescence quenching mechanism arises from either a static mechanism by forming no-fluorescence complexes or a dynamic mechanism by a bimolecular collision of the excited states.[36] In the case of the carbazolyl radical cations, the electrostatic interactions between the TNP anions and carbazolyl radical cations lead to the strong adsorption of TNP anions at the surface of OcCz-PAC nanospheres. As Figure 5b shows, the fluorescent decay curves of OcCz-PAC nanospheres have almost no change either in absence (3.81 ns) or presence (3.39 ns) of TNP. This result indicates that static quenching is a predominant process.[37] In other words, the no-fluorescence complexes created by the electrostatic bound between carbazolyl cations and TNP anions quench the fluorescence emission of OcCz-PAC nanospheres.

Insert Figure 5

4. Conclusions

In summary, we have designed and synthesized a carbazole-type molecule, which demonstrates light-triggered self-assembly into nanospheres. These nanospheres are stable in

various solvents and exhibits green fluorescence emission. Furthermore, we apply these nanospheres as the fluorescence sensor to TNP with high selectivity and sensitivity, and the limit of detection is 1.2×10^{-7} M. The result causing the remarkable fluorescence quenching of OcCz-PAc nanospheres is attributed to the formation of the no-fluorescence complexes due to the electrostatic interactions.

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Figure 1. ^1H NMR spectra of OcCz-PAC in CDCl_3 (5 mM) before (a) and after (b) exposed to UV light for 600 s. Inset: the chemical formula of OcCz-PAC.

Figure 2. (a) Distributions of dynamic light scattering result of OcCz-PAc (0.25 mM) in CHCl_3 under UV light (365 nm) for 600 s; (b) Image of high resolution-transmission electron microscopy (HR-TEM) of OcCz-PAc nanospheres.

Figure 3. (a) PL spectra of OcCz-PAc in CHCl_3 (10 μM) exposed to UV light (365 nm) from 0 s to 600 s. The excitation wavelength is 340 nm; (b) PL intensities of OcCz-PAc recorded at 391 nm and 494 nm as a function of irradiating time. Inset: (I) and (II) images of OcCz-PAc in CHCl_3 before and after being irradiated to UV light taken under the daylight and UV light (365 nm), respectively.

Figure 4. (a) PL spectra of OcCz-PAc nanospheres (2 μ M) in THF upon gradual addition of TNP from 0 to 1×10^{-4} M; (b) the changes of the fluorescence intensity of OcCz-PAc nanospheres solution as a function of the concentration of TNP solution.

Table 1. Some reported results for the TNP detection in solution.

Sensing materials	Limit of detection	Solvent	Reference
OcCz-PAc nanospheres	1.20×10^{-7} M	THF	This work
Nph-An	4.70×10^{-7} M	THF- Water	[19]
N-acylhydrazone (L)	4.30×10^{-7} M	DMF	[20]
[Zn(PAM)(en)] (1)	2.59×10^{-6} M	DMSO	[21]
Pentacenequinonederivative 3	3.50×10^{-7} M	Toluene/DCM	[22]
bis(8-hydroxyquinoline)- aluminium (Bhq-Al)	2.80×10^{-7} M	Formamide	[23]
DNSA-SQ	0.70×10^{-7} M	CH ₃ CN	[24]
BSA-CuInS ₂	0.28×10^{-7} M	PBS buffer	[25]
(Z)-2-(4-aminophenyl)-3-(4- butoxyphenyl)acrylonitrile (ABA)	2.85×10^{-7} M	THF-Water	[26]
Py-3T-Py (4)	6.21×10^{-7} M	Ethanol	[27]
9-Anthracenecarboxamide (1)	1.00×10^{-6} M	Ethanol	[28]
N-acylhydrazone(1)	1.08×10^{-7} M	DMF	[29]
Glc-DHP	0.94×10^{-6} M	Water	[30]
triphenylene derivatives 5	5×10^{-6} M (14pg/cm ²)	THF- Water	[31]
MoS ₂ QDs	0.95×10^{-7} M	Tris-HCl	[32]
C-dots	0.22×10^{-7} M	Phosphate Buffer	[33]
PyT	5.00×10^{-6} M	CH ₃ CN	[34]
Pentacenequinone (8)	2.50×10^{-7} M	DMSO-Water	[35]