Photorefractive hyper-structured molecular glasses constructed by calix[4]resorcinarene core and carbazole-based methine nonlinear optical chromophore†

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Abstract: Seven *C*-methylcalix[4]resorcinarene (CRA)-based photorefractive (PR) hyper-structured molecular glasses (HSMGs) containing carbazole-based methine nonlinear optical (NLO) chromophores were designed and synthesized via esterification between carboxyl-containing asymmetric CRA core molecule and hydroxyl-containing functional compounds. When the feed ratio of hydroxyl-containing NLO functional compounds to carboxyl groups of CRA-COOH was kept at 1.5/1 by mole, the degree of introduction of NLO chromophore to the CRA core was above 70%. All the HSMGs show low glass transition temperatures (T_g), and good solubility in common low boiling point solvents such as THF, CHCl_3 , *etc.* Powder XRD and UV-vis absorption in films of HSMGs indicate that the aggregation, packing and crystallization of the NLO chromophores in these HSMGs had been effectively reduced. Doping with *N*-ethyl-carbazole (ECz) as a plasticizer and [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) as a photosensitizer, all the HSMGs composites showed good PR effects. All the coupling gain coefficients (Γ) of HSMGs-based composites are about twice to the corresponding small molecular NLO chromophores-based composites, thanks to the decreased NLO chromophores antiparallel packing caused by the asymmetric CRA core. Among them, CRA-CSN/ECz/PCBM (69:30:1, wt.%) composite exhibited the best performance with the Γ value of 78.2 cm^{-1} at the external electric field of $12.5 \text{ V } \mu\text{m}^{-1}$, which is one of the best performance in molecular glasses under the same test conditions. Coupled with their convenient synthesis, this work will provide a new simple design strategy for organic PR materials.

Keywords: organic photorefractive materials, hyper-structured molecular glass, calix[4]resorcinarene, nonlinear optical, methine chromophore

†Electronic Supplementary Information (ESI) available: Synthetic procedures of the five functional compounds and CRA-COOH core molecule; Additional figures of ^1H (^{13}C) NMR, FTIR, GPC, TGA, DSC and UV-vis spectra of functional compounds and HSMGs.

1. Introduction

Photorefractive (PR) effect is seen in some materials that combine photoconductivity and nonlinear optical (NLO) response to modulate the refractive index of the medium,^[1-3] and has attracted great amounts of attention due to their potential applications, such as updatable three-dimensional (3D) holographic display, high-density optical data storage, and optical imaging processing, *etc.*^[3-6] In comparison with traditional inorganic PR materials, the organic ones have become a focus recently due to their benefits like low-cost, ease in processability, and the possibility to tune their properties through modification of chemical or compositional properties, *etc.* Organic PR mechanism (Chart S1, ESI†)^[1-3] indicates that organic PR composites are composed of photoconductors, photosensitizers, NLO chromophores and trapping center. Among various organic PR materials, guest-host systems, prepared by doping small molecular NLO chromophores into polymeric photoconductors, are the most studied for practical application because of their eases of fabrication.^[7, 8] However, with the increasing of NLO chromophore doping concentration, the unfavorable antiparallel packing of chromophores resulting from the strong interchromophore dipole-dipole interactions gradually appeared, leading to a decreased PR effect.^[9] Recently, some nonlinear molecules such as hyper-structured molecules (HSMs),^[10] star-shaped molecules,^[11] dendritic molecules,^[12] *etc.* with three-dimensional (3D) branched structure for reducing the detrimental dipole-dipole interactions, have been designed and synthesized for trying to solve this problem. PR hyper-structured molecular glasses (**HSMGs**) are vitreous state molecules that combine different functional PR components such as charge transporting (CT) groups and NLO chromophores together using various chemical bonds to form a complex molecule, and realize the PR effect through the synergy among the components.^[13] Their unique 3D structures can efficiently prevent the easy packing of NLO chromophores and decrease the crystallization tendency.^[14] Previously in our lab, using cyclotriphosphazene as the core, carbazole as CT units, and carbazole-azo-nitrobenzene as NLO chromophores, two PR **HSMGs** (Chart S2, ESI†) were synthesized by post-functionalization method, and the synthesized HSMG showed good PR performance.^[10] As the small size of cyclotriphosphazene core has high steric hindrance, only one or two NLO chromophores were incorporated into the core. In theory, the NLO effect is proportional to the effective chromophore concentration.^[15, 16] Therefore, it is more meaningful to synthesize **HSMGs** with higher NLO chromophores loading density, which is still a challenging task in this area.

On the other hand, **C-methylcalix[4]resorcinarene (CRA, Chart 1)**^[17, 18] is a macrocyclic compound easily prepared by acid-catalyzed condensation of resorcinol and an acetaldehyde. As the eight hydroxyl (-OH) groups of its cis-cis-cis (ccc) isomer can undergo hydrogen bonding in solid state, it shows quite poor solubility in common organic solvents.^[17] Fortunately, when its eight -OH groups are substituted by other hydrophobic groups like ester groups, ether groups, *etc.*, the intramolecular hydrogen bonds become very weak. As a consequence, the resultant **CRA** derivatives show good solubility caused by their noncentro-symmetric configuration. **CRA** is also a very popular molecular scaffold for the synthesis of functional materials.^[19-24] As the asymmetrical structure and amorphous state^[25] are also benefit for enhancing the orientation of NLO chromophore in PR molecular glasses, it is worth using **CRA** as core to construct **HSMGs**.

In this contribution, **CRA**, with larger size than cyclotriphosphazene, was used as the core to construct PR **HSMGs (Chart 1)**, for trying to decrease the steric hindrance of the introduction of NLO chromophores, and increasing the NLO chromophore contents. The target PR **HSMGs, CRA-NLO**, could be easily prepared through the direct reaction between the core molecule CRA-a and dipolar chromophores NLO-b via esterification, etherification, or click reaction, *etc.* The contents of NLO chromophore in **HSMGs** could be also easily adjusted by controlling the feed

ratio of NLO chromophore and CT compounds. In addition, as the NLO chromophore was synthesized in advance, the problem that two acceptors were introduced into the 3, 6-position of carbazole caused by post-functionalization could be completely avoided. Furthermore, the rigid 3D **CRA** core was helpful for maintaining the amorphous state in **HSMGs** at room temperature ^[11, 26] and decreasing the NLO chromophores antiparallel packing. According to the previous work,^[27, 28] the methine NLO chromophore, with carbazole as donor and a nitrobenzene and a cyano group as acceptor (**Cz-CSN-OH**, **Scheme 1**), was chosen to construct **HSMGs** firstly, due to its better PR performance than the other chromophores. To investigate the influence of NLO chromophore contents on PR performance, four **HSMGs** with different **Cz-CSN** contents were designed and synthesized. As expected, the composite based on **CRA-CSN**, with the highest loading concentration of chromophores, showed the best PR performance with the coupling gain coefficient of 78.2 cm⁻¹ at a relative low external electric field of 12.5 V μm⁻¹, which is one of the best performance in molecular glasses under the same test conditions. Then, the other three **HSMGs** containing different carbazole-based methine chromophores were synthesized, and all of them also showed much better PR performance than their prototype chromophores.

Chart 1, The design idea of CRA-NLO for PR application.

2. Experimental

2.1. Materials

The carboxyl-containing **CRA** derivative, **CRA-COOH**, ^[29, 30] and the hydroxyl-containing functional compounds, **Cz-OH**, ^[31, 32] **Cz-CSN-OH**, ^[33-37] **Cz-SN-OH**, ^[38] **Cz-MN-OH**, ^[28, 38] and **Cz-CMA-OH**, ^[39] were synthesized according to literature procedures. Their chemical structures are shown in **Scheme 1** (for detailed synthesis and data analysis, see ESI†). According to our studies and literatures,^[40, 41] it is very difficult to introduce bulky substituents into **CRA** core through direct reaction between the phenolic hydroxyl groups and substituent precursors owing to the high steric hindrance. Therefore, the upper rim of **CRA** was extended outward for two carbons, which could reduce the steric hindrance on the introduction of bulky NLO chromophores. Meanwhile, the -OH groups of **CRA** were transformed into carboxyl groups (-COOH) for the latter esterification. In addition, all NLO chromophores contain a long flexible alkyl chain, which would increase the flexibility between NLO chromophore and **CRA** core of the resulting **HSMGs**, thus decreasing their glass transition temperature (T_g) and facilitating the chromophore orientational enhancement effect.^[42] For comparison with the PR properties of **HSMGs**, a common NLO chromophore, 4-piperidinobenzylidenemalononitrile (**PDCST**), was also synthesized according to the literature procedure (Scheme S3, Fig. S23, ESI).^[43] 1, 2-Dichloroethane (DCE) was dried over and distilled from CaH₂. Tionyl chloride (SOCl₂) was distilled under constant pressure. Tetrahydrofuran (THF) was purified through distillation over sodium with

benzophenone as an indicator. All other reagents were used as received.

2.2. Instrumentation

Proton nuclear magnetic resonance (^1H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were measured on Bruker DPX-400 spectrometer using tetramethylsilane (TMS) as the internal standard. Elemental analysis (EA) was carried out by using a Vario EL/micro cube elemental analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 460 spectrometer on KBr pellets. [Matrix-assisted laser desorption/ionization time-of-flight mass spectra \(MALDI-TOF MS\) were measured on a Shimadzu Biotech AXIMA Performance 2.9.3.20110624 mass spectrometer in positive ion mode.](#) Gel permeation chromatography (GPC) measurement calibrated with polystyrene standard was performed using THF as eluent at 40 °C on a Waters 515 instrument, and the flow rate was 1 mL min⁻¹. Thermogravimetric analysis (TGA) were performed on a Mettler-Toledo TGA/DSC 1 simultaneous thermal analyzer at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurement was carried out under a nitrogen atmosphere on a TA Q 100 differential scanning calorimeter at a heating rate of 10 °C min⁻¹. UV-vis absorption spectra were obtained using a Shimadzu UV-2401 spectrometer. X-ray diffraction (XRD) analysis was carried out by using a Bruker AXS D8 Advance diffractometer with Cu K α radiation. Melt points were performed on X5A Micro Melting Moint Apparatus (BEIJING FOCUS, China).

2.3. Synthesis

As shown in **Scheme 1**, seven **HSMGs** were synthesized by the esterification between carboxyl-containing CRA core molecule (**CRA-COOH**) and hydroxyl-containing NLO chromophore compounds (**Cz-CSN-OH**, **Cz-SN-OH**, **Cz-MN-OH**, and **Cz-CMA-OH**) with or without a CT compound (**Cz-OH**). All the feed ratio of -OH groups and -COOH was kept at a constant mole ratio of 1.5/1. When the feed ratio of **Cz-SN-OH**, **Cz-SN-OH**, **Cz-MN-OH**, or **Cz-CMA-OH** to -COOH of **CRA-COOH** was kept at 1.5/1 by mole, the corresponding **HSMGs** were named as **CRA-CSN**, **CRA-SN**, **CRA-MN**, and **CRA-CMA**, respectively. When the feed ratio of **Cz-CSN-OH** to -COOH of **CRA-COOH** was kept at 0.25/1, 0.50/1, and 0.75/1, the corresponding **HSMGs** were named as **CRA-CSN_x-Cz_(100-x)** (here, x=25, 50, and 75, is the mole percent of **Cz-CSN-OH** to -COOH of **CRA-COOH**).

Synthesis of CRA-CSN

Thionyl chloride (1 mL) was dropwise added to the mixture of **CRA-COOH** (0.1 mmol, 0.1051g, containing 0.8 mmol -COOH group), DCE (3 mL) and one drop of DMF under nitrogen atmosphere. The mixture was slowly heated to 90 °C, and then stirred for 2 h. The solvent and residual **thionyl chloride** were removed under reduced pressure. Further purification was conducted repeatedly by addition of 10 mL of DCE and evaporation to remove the unreacted **thionyl chloride**, and finally 5 mL of DCE was added to dissolve **CRA-COCl** for next step reaction.

Cz-CSN-OH (1.2 mmol, 0.5291 g), 4-dimethylaminopyridine (**DMAP**, 10 mg) and triethylamine (**TEA**, 0.2 mL) were dissolved in DCE (10 mL). Then **CRA-COCl** (0.1 mmol) in DCE (5 mL) was dropwise added to the reaction mixture cooled with ice-water bath under argon atmosphere. Upon the addition finished, the reaction mixture was heated to reflux and stirred for 24 h. Finally, methanol (1 mL) as blocking agent was added and stirred at room temperature for another 12 h. The mixture was poured into saturated salt solution and extracted with chloroform. The organic layer was washed with water, dried with anhydrous MgSO₄, and concentrated under reduced pressure. The product was purified by column chromatography on silica gel using chloroform/methanol (v/v, 3/1) to obtain an orange solid (0.3257 g, yield=75%). GPC (THF, PS): M_w=5 610, PDI=1.32. ^1H NMR (DMSO- d_6), δ (TMS, ppm): 6.95-9.23 (m, 67.4H, ArH and -C=CH- of Cz-CSN-OH residual moiety), 6.02-6.94 (d, 8H, ArH of CRA-COOH residual moiety),

3.54-5.05 (m, 53.5H), 0.55-2.00 (m, 66.0H). FTIR (KBr pellet, cm^{-1}): 2206 (-CN), 1752 (-C=O), 1652 (-C=C-), 1516, 1340 (-NO₂).

Synthesis of CRA-CSN₇₅-Cz₂₅

Cz-CSN-OH (0.6 mmol, 0.2651 g), **DMAP** (10 mg) and **TEA** (0.2 mL) were dissolved in DCE (8 mL). **CRA-COCl** (0.1 mmol) in DCE (5 mL) was dropwise added to the above mixture cooled with ice-water bath under argon atmosphere. The mixture was heated to reflux, stirred for 12 h, and cooled down to room temperature. Then **Cz-OH** (0.6 mmol, 0.1634 g) in DCE (3 mL) was added, stirred for 12 h, and cooled down again. Finally, methanol (1 mL) was added and stirred for another 12 h. After the same post-treatment process as **CRA-CSN**, an orange solid was obtained (0.2096 g, yield=52%). GPC (THF, PS): M_w =8 650, PDI=1.54. ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 6.85-9.40 (m, 61.7H, ArH and -C=CH- of Cz-CSN-OH residual moiety and ArH of Cz-OH residual moiety), 5.90-6.81 (d, 8H, ArH of CRA-COOH residual moiety), 3.62-5.08 (m, 32.3H), 0.46-1.86 (m, 74.7H). FTIR (KBr pellet, cm^{-1}): 2208 (-CN), 1752 (-C=O), 1650 (-C=C-), 1515, 1342 (-NO₂).

Synthesis of CRA-CSN₅₀-Cz₅₀

In a same procedure with **CRA-CSN₇₅-Cz₂₅**, **CRA-CSN₅₀-Cz₅₀** was synthesized from **Cz-CSN-OH** (0.4 mmol, 0.1767 g), **Cz-OH** (0.8 mmol, 0.2178 g) and **CRA-COOH** (0.1 mmol, 0.1051g) to obtain a yellow solid (0.1875 g, yield=52%). GPC (THF, PS): M_w =11 500, PDI=2.03. ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 6.85-9.40 (m, 66.4H, ArH and -C=CH- of Cz-CSN-OH residual moiety and ArH of Cz-OH residual moiety), 5.90-6.81 (d, 8H, ArH of CRA-COOH residual moiety), 3.62-5.08 (m, 38.0H), 0.46-1.86 (m, 89.2H). FTIR (KBr pellet, cm^{-1}): 2208 (-CN), 1750 (-C=O), 1652 (-C=C-), 1514, 1339 (-NO₂).

Synthesis of CRA-CSN₂₅-Cz₇₅

In a same procedure with **CRA-CSN₇₅-Cz₂₅**, **CRA-CSN₂₅-Cz₇₅** was synthesized from **Cz-CSN-OH** (0.2 mmol, 0.0884 g), **Cz-OH** (0.8 mmol, 0.2723 g) and **CRA-COOH** (0.1 mmol, 0.1051g) to obtain a pale yellow solid (0.1089 g, yield=33%). GPC (THF, PS): M_w =6 410, PDI=1.52. ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 6.85-9.40 (m, 52.6H, ArH and -C=CH- of Cz-CSN-OH residual moiety and ArH of Cz-OH residual moiety), 5.90-6.81(d, 8H, ArH of CRA-COOH residual moiety), 3.62-5.08 (m, 32.5H). FTIR (KBr pellet, cm^{-1}): 2208 (-CN), 1752 (-C=O), 1629 (-C=C-), 1515, 1345 (-NO₂).

Synthesis of CRA-SN

In a same procedure with **CRA-CSN**, **CRA-SN** was synthesized from **Cz-SN-OH** (1.2 mmol, 0.5103 g) and **CRA-COOH** (0.1 mmol, 0.1051g) to afford a red solid (0.3798 g, yield=90%). GPC (THF, PS): M_w =5 580, PDI=1.23. ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 7.07-8.66 (m, 84.1H, ArH and -CH=CH- of Cz-SN-OH residual moiety), 6.09-7.02 (d, 8H, ArH of CRA-COOH residual moiety), 3.66-4.88 (m, 42.4H), 0.92-1.77 (m, 74.1H). FTIR (KBr pellet, cm^{-1}): 1753 (-C=O), 1622 (-C=C-), 1508, 1336 (-NO₂).

Synthesis of CRA-MN

In a same procedure with **CRA-CSN**, **CRA-MN** was synthesized from **Cz-MN-OH** (1.2 mmol, 0.4159 g) and **CRA-COOH** (0.1 mmol, 0.1051g) to afford a yellow solid (0.2229 g, yield=61%). GPC (THF, PS): M_w =8 520, PDI=1.76. ¹H NMR (DMSO-*d*₆), δ (TMS, ppm): 7.04-8.93 (m, 47.6H, ArH and -CH=C- of Cz-MN-OH residual moiety), 6.09-7.02 (d, 8H, ArH of CRA-COOH residual moiety), 3.56-5.15 (m, 38.3H), 0.89-1.94 (m, 75.8H). FTIR (KBr pellet, cm^{-1}): 1753 (-C=O), 1622 (C=C), 1508, 1336 (-NO₂).

Synthesis of CRA-CMA

In a same procedure with **CRA-CSN**, **CRA-CMA** was synthesized from **Cz-CMA-OH** (1.2 mmol, 0.4605 g) and

CRA-COOH (0.1 mmol, 0.1051g) to afford a yellow solid (0.3243 g, yield=82%). GPC (THF, PS): $M_w=5\ 150$, $PDI=1.33$. 1H NMR (DMSO- d_6), δ (TMS, ppm): 7.11-8.98 (m, 57.3H, ArH and -CH=C- of Cz-CMA-OH residual moiety), 5.99-7.04 (d, 8H, ArH of CRA-COOH residual moiety), 3.66-4.81 (m, 68.4H), 0.92-1.83 (m, 76.4H). FTIR (KBr pellet, cm^{-1}): 2216 (-CN), 1725 (-C=O), 1626 (-C=C-).

2.4. PR device fabrication and TBC measurement

Thin films for TBC measurements were fabricated by a simple solution casting. Indium tin oxide (ITO, square resistance $\leq 10\ \Omega$) were cleaned by washing with acetone, distilled water and THF sequentially in an ultrasonic bath before use. The PR sample, *N*-ethyl carbazole (**ECz**) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (**PCBM**) were simultaneously dissolved in THF and then filtered through a 0.2 μm pore Teflon membrane filter. The filtrated solution was dropped onto two ITO glass plates at room temperature. Residual solvent was removed under vacuum for 12 h. The dried film was heated above T_g on a hot plate, and then sandwiched between two ITO glass plates by applying gentle pressure. The sandwich was cooled quickly to room temperature while maintained under pressure and the thickness of the film was controlled to be 80 μm through a Teflon spacer.

The illustrative experimental setup for TBC measurement is shown in **Fig. 1**. Two coherent *p*-polarized He-Ne laser beams at a wavelength of 633 nm were overlapped inside the sample to produce an interference pattern. The normal of the sample surface was tilted at an external angle $\phi_{ext} = 45^\circ$ with respect to the symmetric axis of the two incident beams, and the angle between two writing beams $2\theta_{ext} = 20^\circ$. K is the grating wave vector. V is an applied external electric field. In the TBC experiment, the initial power of two writing beams (beam 1 and beam 2) was 8 and 16 mW, respectively. The TBC coupling gain coefficient (Γ , cm^{-1}) was estimated by the following expression^[10, 44]:

$$\Gamma = \frac{\cos\theta_{in}}{d} \ln(\gamma_0\beta) - \ln(\beta + 1 - \gamma_0)$$

where, d is the sample thickness, ϕ_{in} is the incident angle of the beam 1 inside the sample, β is the initial intensity ratio of beams after the sample in the absence of coupling, and γ_0 is the beam-coupling ratio ($\gamma_0=I/I_0$). Here, I_0 is the signal intensity without the pump beam. I is the signal intensity with the pump beam.

Fig. 1, Illustration of the experimental setup for two-beam coupling (TBC) measurement.

3. Results and discussion

3.1. Synthesis and characterization

As shown in **Scheme 1**, seven **HSMGs** were synthesized by esterification between carboxyl-containing CRA core molecule (**CRA-COOH**) and hydroxyl-containing NLO chromophore compounds (**Cz-CSN-OH**, **Cz-SN-OH**, **Cz-**

MN-OH, and Cz-CMA-OH) with or without a CT compound (Cz-OH) in DCE using DMAP as the catalyst and TEA as the deacid reagent. In order to increase the esterification reactivity, the carboxyl groups of CRA-COOH were transformed into acyl chloride groups beforehand. As the boiling point of DCE is slightly higher than that of thionyl chloride, the solvent and residual thionyl chloride could be removed under reduced pressure. Then, further purification could be conducted repeatedly by addition of DCE and evaporation to remove the unreacted thionyl chloride. More importantly, all the raw materials (CRA-COCl, NLO-OH and Cz-OH) and products (seven HSMGs) of esterification exhibited good solubility in DCE. In order to obtain HSMGs with high degree of esterification, the feed ratio of hydroxyl groups and carboxyl groups was kept at a constant mole ratio of 1.5/1, and a little methanol was added at last. All the products were purified by column chromatography on silica gel using chloroform/methanol in different volume ratio as eluent.

Scheme 1, Synthetic routes of seven HSMGs.

The chemical structures of HSMGs were confirmed by ^1H NMR and FTIR. Here, CRA-CSN is used as an example to illustrate the successful synthesis. Compared the ^1H NMR spectrum of CRA-CSN with those of CRA-COOH and Cz-CSN-OH (Fig. 2), it could be inferred that the multi-peaks in the range of 6.95-9.23 ppm originated from aromatic protons and carbon-carbon double bond protons of the Cz-CSN-OH residual moieties, and two peaks in the range of 6.02-6.94 ppm originated from the aromatic protons of the CRA-COOH residual moieties. When the functional groups were connected to the CRA core molecule, the substituent groups could reduce the flexibility of the ccc isomers, and the corresponding CRA derivatives were composed of several configurations, which gave rise to broader resonances of aromatic protons and $\text{CH}_3\text{CH}-$ of the CRA-COOH residual moieties. [45] The protons signal of $-\text{OCH}_3$ (3.67 ppm) in CRA-CSN was very weak, indicating only a little blocking agent methanol was incorporated into CRA core. The successful synthesis of CRA-CSN could also be confirmed by its FTIR spectrum (Fig. S16a, ESI†). The peaks of $-\text{CN}$ (2206 cm^{-1}) and ester groups (1752 cm^{-1}), originating from Cz-CSN-OH and CRA-COOH residual moieties, respectively, could be observed in the CRA-CSN FTIR spectrum. Compared with the stretching vibration peaks of $-\text{OH}$ (Cz-CSN-OH) and $-\text{COOH}$ (CRA-COOH), the peaks around 3400 cm^{-1} of CRA-CSN became much weaker.

Fig. 2. ^1H NMR spectra of CRA-CSN, Cz-CSN-OH and CRA-COOH.

Table 1. Some characterization data and TBC gain coefficients of HSMGs.

HSMGs	M_w ^a	M_w/M_n ^a	D.I. ^b (%)	T_d ^d (°C)	T_g ^e (°C)	λ_{max} /FWHM in solution ^f (nm)	λ_{max} /FWHM in films ^f (nm)	Γ ^g (cm^{-1})
CRA-CSN	5 610	1.32	70.1	285.4	53.1	422/81	436/114	78.2
CRA-CSN ₇₅ -Cz ₂₅	8 650	1.54	- ^c	246.0	50.4	422/81	430/99	68.4
CRA-CSN ₅₀ -Cz ₅₀	11 500	2.03	-	224.4	50.1	422/83	431/99	46.9
CRA-CSN ₂₅ -Cz ₇₅	6 410	1.52	-	201.7	47.3	422/83	434/112	28.1
CRA-SN	5 580	1.23	80.7	283.6	49.5	414/88	425/122	20.3
CRA-MN	8 520	1.76	74.4	266.2	57.1	410/56	424/78	32.8
CRA-CMA	5 150	1.33	89.5	226.3	48.1	402/55	404/74	55.5

^a Determined by GPC in THF solvent on the basis of a polystyrene calibration. ^b The degree of introduction (D.I.) of NLO chromophore to the CRA core molecule calculated from ^1H NMR. ^c Undetermined. ^d The 5% weight loss temperature of HSMGs detected by TGA analysis under nitrogen. ^e The glass transition temperature detected by DSC analysis under nitrogen. ^f The maximum absorption wavelength (λ_{max}) and full width at half maximum (FWHM) of HSMGs in chloroform solution and in films. ^g The TBC coupling gain coefficients of HSMGs/ECz/PCBM (69:30:1, wt.%) composite at the external electric field of $12.5 \text{ V } \mu\text{m}^{-1}$.

The weight average molecular weights (M_w) and polydispersity index (PDI) measured by GPC of HSMGs were in the range of 5.61×10^3 – 11.5×10^3 and 1.23–2.03, respectively. The GPC curves could be seen in Fig. 3, and the GPC data are summarized in Table 1. Their molecular weights measured by GPC method showed a large deviation from the theoretical values, which should be caused by the differences between the linear structure of GPC calibration standards and the 3D structure of HSMGs.^[46] In addition, using the aromatic protons of CRA core as an internal standard, the average degree of introductions (D.I.) of NLO chromophore to CRA core could be estimated by the integrated values of aromatic protons and double bond protons of NLO-OH residual moieties. Using CRA-CSN as an example, the detailed calculation process is shown in Fig. S15 (ESI[†]). The D.I. estimated by ^1H NMR of CRA-CSN, CRA-SN, CRA-MN and CRA-CMA were 70.1%, 80.7%, 74.4%, and 89.5%, respectively, indicating that 5–7 carboxyl groups of the total 8 carboxyl groups in CRA-COOH had reacted with NLO-OH in the obtained HSMGs. These results are also consistent with the MALDI-TOF MS spectra of CRA-CSN and CRA-SN (Fig. S17, ESI[†]). The MALDI-TOF MS results indicated that CRA-CSN was composed of several CRA-CSN derivatives containing 5, 6, and 7 CzCSN-substituents. Compared with the cyclotriphosphazene-based HSMGs with D.I. values of 16.7% or 33.3%,^[10] the NLO

chromophore **D.I.** of as-prepared CRA-based **HSMGs** significantly increased. As **CRA-CSN_x-Cz_(100-x)** (here, $x=25, 50$ and 75) have two kinds of arms, it is difficult to calculate their NLO chromophore **D.I.** according to ^1H NMR spectra. Nevertheless, their ^1H NMR spectra (Fig. S11, ESI †), TGA data (Fig. S19a, ESI †) and UV-vis absorption spectra (Fig. 5) did indicate that the **Cz-CSN** contents of resultant **HSMGs** increased with the fed **Cz-CSN-OH** increase, which will be discussed later.

Fig. 3, GPC chromatograms of **HSMGs**.

3.2. Solubility and crystallinity

Solubility is an important requirement for organic PR materials because the devices are fabricated by solution casting. The solubility was tested at room temperature. Unlike **CRA-COOH** core molecule, which almost cannot be soluble in common organic solvents owing to the strong hydrogen bonds caused by carboxyl groups, all seven **HSMGs** show good solubility in some common solvents, such as THF, chloroform (CHCl_3), CH_2Cl_2 , N, N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO), *etc.*, showing advantages of the asymmetric structure of CRA core and the long alkyl flexible linkage between CRA and NLO chromophores. Hence, the UV-vis absorption spectra in films and optical films for PR measurement were fabricated through spin-coating from chloroform solution, and solution casting from their THF solution, respectively.

As non-crystalline materials are required for achieving good performance for PR devices, and low molecular organic compounds are easily to crystallize in solid state, a major challenge in developing molecular glass PR materials is how to make the low molecular weight organics form a stable amorphous phase at room temperature. [47] The amorphous character of **Cz-CSN-OH** and some **HSMGs** were characterized by using XRD analysis. As shown in Fig. S18 (ESI †), the sharp and strong peaks of **Cz-CSN-OH** revealed its high crystallinity, and the broad and weak signals of **HSMGs** demonstrated their amorphous states. The amorphous nature of **HSMGs** are caused by the asymmetric structure of **CRA** derivatives containing bulky substituent groups, [26, 45] which represented that the introduction of NLO chromophores into **CRA** core molecule could effectively avoid the crystallization of NLO chromophores. The amorphous states of **HSMGs** are helpful to improving their PR properties.

3.2. Thermal stability

TGA and DSC were used to investigate the thermal stability of **HSMGs**. The thermal decomposition temperatures

(T_d) obtained from TGA and the glass transition temperatures (T_g) obtained from DSC are summarized in **Table 1**. TGA curves of **CRA-CSN** and **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75) are shown in **Fig. S19a (ESI†)**. Among them, **CRA-CSN** showed the highest T_d , implying that the T_d of **HSMGs** would increase with the increase of **Cz-CSN** contents. With the feed ratio x in the former preparation of **HSMGs** increased, the T_d s of **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75) gradually increased, indicating the contents of NLO chromophores in **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75) did increase with the increase of x . The DSC curves of **CRA-CSN** and **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75) are given in **Fig. S19b (ESI†)**. As there exists several kinds of segments in **HSMGs**, they showed two or three transition temperatures. All the **HSMGs** showed a T_g in the range of 47-53 °C, which could be attributed to the motion of NLO chromophore-based segments. Compared the DSC curve of **CRA-CSN₂₅-Cz₇₅** with that of **CRA-CSN**, an additional T_g (27.4 °C) of **CRA-CSN₂₅-Cz₇₅** could be assigned to the motion of carbazole-based segments. In comparison with **HSMGs** constructed by cyclotriphosphazene core and ethyl linkage in our previous work,^[10] due to the long flexible linkage between the asymmetric **CRA** core and NLO chromophores, the T_g values of these **HSMGs** obviously decrease, facilitating NLO chromophore orientational enhancement effects, which is beneficial to improving PR performance.^[48]

3.3. UV-vis absorption properties

UV-vis absorption of **CRA-CSN** and **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75) were measured in **chloroform** solution (0.03 mg mL⁻¹) and in films on quartz glass. The films were prepared by spin-coating **HSMGs** chloroform solution (5 mg mL⁻¹) onto quartz glass at a speed of 1500 rpm at room temperature, and dried under vacuum at 35 °C. The maximum absorption wavelength (λ_{max}) and full width at half maximum (FWHM) are summarized in **Table 1**.

UV-vis spectra of **CRA-CSN**, **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75), and **Cz-CSN-OH** in **chloroform** solutions are given in **Fig. 5a**. As for **CRA-MBA** without NLO chromophore, no absorption peak was observed in the visible region. While all of the **Cz-CSN**-containing **HSMGs** and **Cz-CSN-OH** showed similar absorption bands in the range of 360-520 nm centered at 422 nm, which could be attributed to the absorption of charge transfer from electron-donating carbazole moieties to electron-withdrawing cyano groups and nitrobenzene moieties through methine bridge.^[49] Furthermore, with the feed ratio x in the former preparation of **HSMGs** increased, this peak absorbance of **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75) at the same concentration gradually increased, which also indicated that **Cz-CSN** contents in **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75) did increase with the increase of x . Simultaneously, the content of NLO chromophore almost did not affect their λ_{max} position and FWHM in dilute solution, which suggested that the intramolecular influence of chromophores in **HSMGs** was weak in dilute solution. In addition, the maximum absorption peaks of **CRA-SN**, **CRA-MN** and **CRA-CMA** in **chloroform** solution were at 414, 410 and 402 nm (**Fig. S21a, ESI†**), respectively. From **CRA-CSN** to **CRA-CMA**, with the electron-withdrawing ability of acceptor in the chromophore increase, the absorption maximum had gradually red-shifted because the absorption peak position of chromophore depends on the dipole strength between carbazole nucleus and electron-withdrawing moieties.^[49] **Fig. 5b** shows the UV-vis spectra of **CRA-CSN**, **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75), and **Cz-CSN-OH** in films. The peak shape corresponding to NLO chromophore of **Cz-CSN-OH** in film was quite different from that in solution centered at 423 nm due to the aggregation, packing and crystallization of NLO chromophores. While for **Cz-CSN**-based **HSMGs**, their shape of peaks corresponding to NLO chromophores were almost as same as those in solutions, and only about 4-14 nm red-shift of the absorption maximum were observed, which meant that the attachment of NLO chromophores to the asymmetric **CRA** core molecule can effectively decrease the aggregation, packing and crystallization of NLO chromophores, which is helpful to improving their PR properties. The amorphous state of **HSMGs** had already been

confirmed by their XRD analyses (Fig. S18, ESI†).

Fig. 5, Normalized UV-vis spectra of CRA-CSN, CRA-CSN_x-Cz_(100-x) (x=25, 50, and 75), and Cz-CSN-OH (a) in chloroform solution (0.03 mg/mL) and (b) in films on quartz glass.

3.4. Photorefractive properties

The PR performance could be investigated by two-beam coupling (TBC) and four-wave mixing (FWM) experiments. FWM provides information about the amplitudes of the PR space-charge field and of the resulting refractive index modulation. And asymmetric TBC is the real proof of PR effect, which can rule out other possible grating forming mechanisms as photochromic or thermal grating.^[50] Therefore, the PR effects of **HSMGs** were investigated by TBC experiments.

As T_g s of **HSMGs** were still higher than room temperature, the test condition, **ECz** was used as a plasticizer to reduce the T_g s of the **HSMGs** composite films. According to the T_g value of **CRA-CSN/ECz** composite, the content of **ECz** was determined to be 30 wt.%, and the T_g value of corresponding **CRA-CSN/ECz** (69:30, wt.%) composite was 16.6 °C (Fig. S22, ESI†). In addition, **ECz** could also serve as a photoconductor because of its good hole-transporting ability.^[1, 2] Moreover, **PCBM**, a C₆₀ derivative, was used as a sensitizer. In several studies exploring the contribution of a sensitizer to the PR performance, various characteristics (*e.g.*, photoconductivity, TBC gain, *etc.*) were measured as a function of the sensitizer concentration, and addition of up to 1 wt.% of a sensitizer led to a significant improvement of PR performance.^[51, 52] Therefore, 1 wt.% of **PCBM** was also adopted in this work without further optimization. **Fig. 6a** shows the chemical structures of **ECz**, **PCBM** and UV-vis absorption spectra of the **CRA-CSN**-based composite films.

All the composite films for PR measurements with the components of **HSMGs/ECz/PCBM**=69:30:1(wt.%) were fabricated through solution casting, and the thickness of films are about 80 μm controlled through a Teflon spacer. The composite films were directly used for PR measurements without pre-poling. The TBC experiments were explored under the irradiation of two beams light with the wavelength of 633 nm, and the coupling gain coefficients (Γ) are summarized in **Table 1**. As shown in **Fig. 6b**, for **CRA-CSN**-based composite, the efficient energy transfer from beam 2 to beam 1 was observed, and its Γ value was calculated as 78.2 cm⁻¹ at the external electric field of 12.5 V μm⁻¹. Generally, the Γ values of organic PR materials (except organic crystals) increase with the increase of external electric field up to 60-80 μm⁻¹. However, in these materials, a trade-off between the magnitude of the applied field with respect to the enhancement of field-dependent effects and the operational lifetime of sample exists.^[1] From the viewpoint of application, a relative low external electric field of 12.5 V μm⁻¹ was applied in our study. The obtained Γ value (78.2 cm⁻¹) of **CRA-CSN**-based composite is one of the best performance in molecular glasses under the similar test

conditions. Under the same measurement conditions, a common NLO chromophore, **PDCST**-based composite with the component of **PDCST/PVK/ECz/PCBM=30:54:15:1(wt.%)** had a Γ value of 26.8 cm^{-1} .^[53, 54] **Fig. 6c** shows the Γ values of **CRA-CSN**, **CRA-CSN_x-Cz_(100-x)** ($x=25, 50$, and 75) and **Cz-CSN-OH** composite films. As expected, with the increase of NLO chromophore contents in **HSMGs**, their Γ values did increase, being in accordance with our previous work.^[10] Furthermore, the Γ value of **CRA-CSN** composite film was 2.75 times that of the corresponding functional compound **Cz-CSN-OH**. On the other hand, the Γ values of **CRA-SN**, **CRA-MN** and **CRA-CMA** were 1.98, 2.57 and 2.49 times that of the corresponding NLO functional compounds composite films (**Fig. 6d**), respectively. The higher PR effects in as-prepared **HSMGs** may result from the asymmetric structure **CRA** core molecule could decrease the antiparallel packing of chromophores, decreasing the interchromophore dipole-dipole interactions, thus enhancing the orientation ability of dipole at electric field.

Fig. 6. (a) UV-vis absorption spectra of CRA-CSN-based composites in films. (b) Energy transfer curves of CRA-CSN composite in TBC experiments at the external electric field of $12.5 \text{ V}\mu\text{m}^{-1}$. (c) The coupling gain coefficients of CRA-CSN, CRA-CSN_x-Cz_(100-x) ($x=25, 50$, and 75), and Cz-CSN-OH composite films. (d) The coupling gain coefficients of CRA-SN, CRA-MN, CRA-CMA and corresponding NLO functional compound composite films.

4. Conclusions

In summary, seven **CRA**-based PR **HSMGs** containing methine NLO chromophores with/without carbazole CT moieties were designed and successfully synthesized by the esterification between carboxyl-containing core molecule and hydroxyl-containing functional compounds. When the feed ratio of hydroxyl-containing NLO functional compounds to carboxyl groups of **CRA-COOH** was kept at 1.5/1 by mole, the **D.I.** of NLO chromophore to the **CRA** core was above 70%, which was much higher than the D.I. (33.3%) of our previous cyclotriphosphazene-based **HSMGs** prepared through post-functionalization.^[10] Doped with **ECz** as a plasticizer and **PCBM** as a photosensitizer, all **HSMGs**-based composite showed good PR effects. The Γ values of **CRA-CSN**, **CRA-SN**, **CRA-MN** and **CRA-CMA** were 2.74, 1.98, 2.57 and 2.49 times that of the corresponding NLO functional compounds composite films, which could be attributed to the asymmetric structure **CRA** core with the decrease of the antiparallel packing of chromophores, thus enhancing the orientation ability of dipole at electric field. Among them, **CRA-CSN**-based composite exhibited the best performance with the Γ value of 78.2 cm⁻¹ at the external electric field of 12.5 V μm^{-1} , which is also one of the best performance in molecular glasses under the same test conditions. Taking into account of the convenient synthesis and effective avoidance of chromophores aggregation, this work will provide a new simple design strategy for organic PR materials.

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