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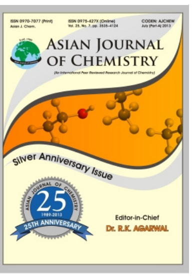

A Study of the Fluorescence Properties of 1,8-Naphthalimide Derivative and CPA Composite

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In this study, to obtain more bulky molecules, change the conjugation length and reduce propensity of concentration quenching, 4-[2,4-di(*tert*-butyl)]phenoxy-N-(2-hydroxyethyl)-1,8-naphthalimide(1,8-naphthalimde derivative) was synthesized. An appropriate polymer as main chain was prepared as well. A series of polymer (N-CPA) with different ratio of 1,8-naphthalimide derivative were synthesized, N-CPA was investigated optically using photoluminescence spectroscopy. As the proportion of 1,8-naphthalimide derivative rose, the fluorescence quenching was advanced. Furthermore, the synthesized polymer was appropriate for forming thin film deposition from dilute polymer solution and the films were fully characterized by UV-visible spectroscopy and photoluminescence spectroscopy. The data of photoluminescence emission peaks, show pure blue photoluminescence both in solution and solid films with λ PLmax locating at 445 nm around and relative narrow FWHM of 38-72 nm. But show red-shift in solid film compare to in solution.

Key Words: 1,8-Naphthalimide derivative, Composite, Blue light-emission, Fluorescence, Free redical polymerization, Synthesis.

INTRODUCTION

Owing to their good optical, thermal and chemical stabilities, high photoluminescence (PL) quantum efficiency in solution[1-4], as well as their potential application of the flat panel displays and solid-state light sources, 1,8-naphthalimide derivatives have attracted much interest for many years. By introducing different electron-donating substituents, such as C-substituted groups[5-7], N-substituted groups[8,9] and O-substituted groups[10], in the 4-position of 1,8-naphthalimides, their photoluminescence emission colour can be commonly tuned from yellowish green to pure blue. In order to exploit blue-emitting photoluminescence materials with reduced propensity of concentration quenching, rigid phenoxy substituents were located at the 4-position of naphthalimides[10] and *tert*-butyl substituents were located at 2 and 4 positions of the phenoxy groups to obtain more bulky molecules and change the conjugation length as well.

It makes great significant that 1,8-naphthalimide derivative compound is attached to polymer *via* grafting reaction to produce novel composite material with remarkable luminescence characteristics, in addition, to prepare neat solid film luminescence apparatus from the former.

It is indispensable to select an appropriate polymer as backbone for the synthesis of these novel 1,8-naphthalimide derivative-containing functional polymers. Polymer matrices whose sides could introduce small molecules principally are polycarbonate (PC), polystyrene (PS), polymethyl methacrylate (PMMA), *etc*. In this work, with the purpose of connecting with novel 1,8-naphthalimide derivative's hydroxyl functional group, isocyanato functional groups of TDI were introduced, moreover, there must be a reactive group in the polymer matrix, for instance hydroxyl or amino-group. A copolymer (CPA), synthesized with methyl methacrylate (MMA), *n*-butyl acrylate (BA) and 2-hydroxyethyl acrylate (HEA), was selected to be the grafting main chain due to modified 1,8-naphthalimide derivative could be attached on it by the reacting of hydroxyl and isocyanato. PMMA has well film-forming property and the flexibility of the film would be good too.

In this study, to take full advantage of the predominant luminescence characteristics possessed by 1,8-naphthalimide derivative compound, 4-[2,4-di(*tert*-butyl)]phenoxy-N-(2-hydroxyethyl)-1,8-naphthalimide was grafted on the main chain of CPA by twice reaction to form luminescence polymers with different proportions of 1,8-naphthalimide derivative on the side-chain. The 1,8-naphthalimide derivative-containing polymer (N-CPA) was a new-style flexible and high luminescent efficiency composite material. Investigate was conducted in our laboratory for the synthesis of novel blue-emitting photoluminescence materials, which was a polymer with 1,8-naphthalimide derivative side-chain. It is make great significance for the studying on luminescent materials.

EXPERIMENTAL

Methyl methacrylate (MMA), *n*-butyl acrylate (BA) and 2-hydroxyethyl acrylate (HEA) were purchased from Beijing East Chemical Industry Factory, distilled before use. 4-Bromo-1,8-naphthalic anhydride and 2,4-di(*tert*-butyl)phenol were supplied by the laboratory of Yan Huang and were used without further purification. Analytically pure azo*bis*isobutyronitrile (AIBN), toluene, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dibutyltin dilaurate (DBTDL), ethanolamine, ethyl acetate (EA), petroleum ether (PE) and toluene diisocyanate (TDI) were supplied by Chengdu Kelong Chemical and Technology Reagents (Chengdu, China). The solvents were of analytical grade and freshly distilled before use. Dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) were dried with CaH_2 and freshly distilled before use.

^{1}H and ^{13}C NMR spectra were recorded on a BRUKER (AVII-400) spectrometer in $CDCl_3$ using TMS as internal standard. High resolution TOF-MS spectra were recorded on a Waters Q-TOF-Pre-miter instrument. A differential scanning calorimeter (DSC) (200 PC, netzsch, Germany). A high performance liquid chromatography (HP1100, Agilent, USA). A Nicolet 1700SX Fourier transform infrared spectrometer (all samples grounded in KBr). A fluorescence spectrophotometer (Hitachi F-7000, Japan) were employed in this work.

Syntheses: The synthetic route to the objective polymer is shown in Fig. 1. Intermediate 2 was prepared according to the previous literatures procedure[11]. Compound **3** (1,8-naphthalimide derivative) was synthesized *via* nucleophilic substitution reaction of phenol and substituted phenol with **2**; CPA was synthesized by free redical polymerization, target product **4** was obtained by twice reactions of -OH and -NCO.

Acrylate multipolymers (CPA): To a solution of methyl methacrylate (MMA), *n*-butyl acrylate (BA), 2-hydroxyethyl acrylate (HEA) and initiator azodiisobutyronitrile (AIBN) dissolved in 50 mL of anhydrous toluene according to the Table-1. After toluene was refluxed at 60 ºC for some time, the starting mixture was fed continuously into the flask using dropping funnel and finished in two hours, continued to reflux 1 h. Colourless transparent and sticky CPA was synthesized in this way. The resultant products have well film-forming characteristic.

TABLE-1
COMPONENTS USED FOR CPA EXPERIMENTS

Polymer	MMA (g)	BA (g)	HEA (g)	AIBN (g)	HEA (%)
CPA_1	6	3	1	0.1	10
CPA_2	6	3	2	0.1	18
CPA_3	6	3	3	0.1	25

4-[2,4-Di(*tert*-butyl)]phenoxy-N-(2-hydroxyethyl)-1,8-naphthalimide: To a solution of 2,4-di(*tert*-butyl)phenol 3.41 g (16.6 mmol) in 40 mL of anhydrous DMSO was added 1.65 g (29.5 mmol) potassium hydroxide. The resulting mixture was stirred at room temperature for 1.5 h under protection of argon, then a solution of 5.28 g (16.5 mmol) 4-bromo-N-(2-hydroxyethyl)-1,8-naphthalimide dissolved in 200 mL DMSO was added dropwise over 0.5 h. The mixture was stirred at room temperature for 8 h, neutralized to pH = 7 with 1 mol L^{-1} hydrochloric acid and then extracted with 20 mL × 3 EA. The organic layer was washed with water twice, dried under anhydrous sodium sulfate, then vacuum-vaporized to remove solvent. The rough product was purified by column chromatograph (PE/EA = 2/1) to obtain pale yellow solid. Yield: 27 %. m.p. 160-162 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.76-8.74 (m, 1H), 8.70-8.68 (m, 1H), 8.48 (d, *J* =8.4 Hz, 1H), 7.81(t, *J* = 8.4 Hz, 1H), 7.54 (s, 1H), 7.30-7.27 (m, 1H), 6.93 (t, *J* = 8.4 Hz, 2H), 4.47 (t, *J* = 5.2 Hz, 2H), 3.98 (t, *J* = 5.2 Hz, 2H), 1.38 (d, *J* = 9.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.35, 164.77, 160.58, 150.77, 148.32, 141.09, 133.44, 132.20, 129.87, 129.01, 126.57, 124.92, 124.56, 124.10, 122.38, 121.45, 115.64, 110.62, 62.06, 42.77, 34.99, 34.80, 31.55, 30.50; TOF-MS: m/z 446.2299 (M + 1), Calcd. (%) for MW: 446.2331.

Graft of 1,8-naphthalimide derivative onto CPA to synthesize N-CPA: To a solution of CPA1 1 g in 20 mL of anhydrous THF was added 120 µL TDI. The starting materials were stirred at 30 ºC for 3 h. Then 0.38 g 1,8-naphthalimide derivative and 50 µL DBTDL was added in the starting materials. The resulting mixture was refluxed at 50 ºC for 5 h. Brown-yellow transparent and sticky N-CPA1 was prepared in this way. The products have well film-forming characteristic, too. The synthesis of $N-CPA_2$ and $N-CPA_3$ in accordance with the above way.

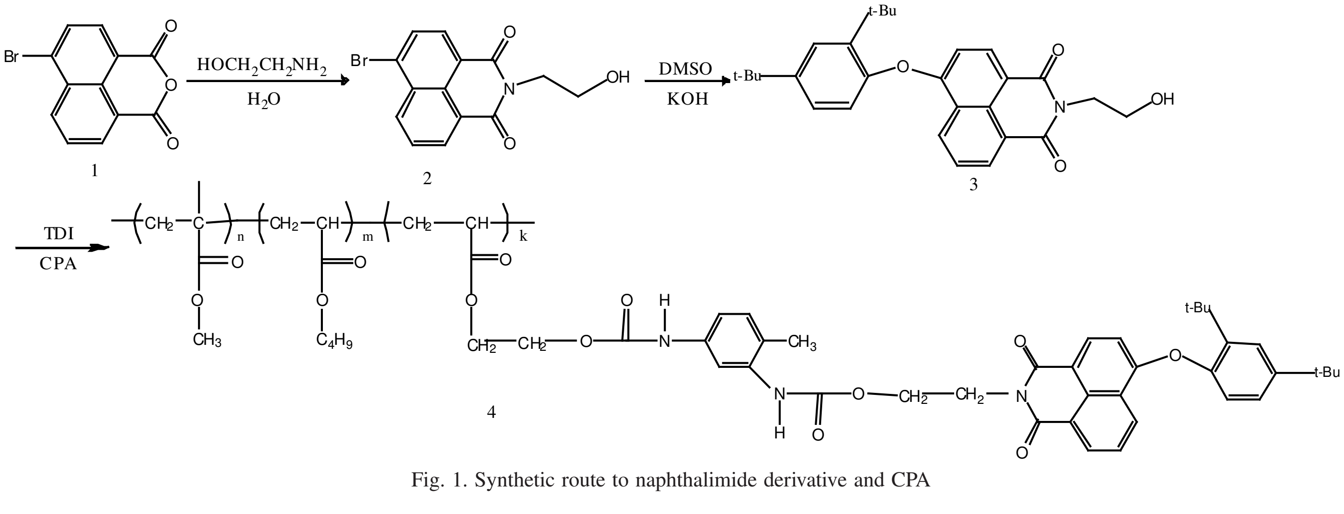

Fig. 1. Synthetic route to naphthalimide derivative and CPA

RESULTS AND DISCUSSION

Synthesis and characterization: 1,8-Naphthalimide derivative is synthesized by means of nucleophilic substitution of phenol derivative with 4-bromo-1,8-naphthalimide, while could not be obtained with satisfied yields, because 2,4-di(*tert*-butyl)phenol as the nucleophilic reagents have lager steric hindrance. The chemical structure of the 1,8-naphthalimide derivative is demonstrated by ^{1}H NMR, ^{13}C NMR and high resolution TOF-MS spectra. 1,8-Naphthalimide derivative and N-CPA can dissolve in many common organic solvents, such as dichloromethane, chloroform, THF, chlorobenzene and toluene.

FTIR spectra of CPA, CPA + TDI, N-CPA and N(1,8-naphthalimide derivative): The FTIR spectra of CPA and CPA + TDI are presented in Fig. 2a, N-CPA is presented in Fig. 2a-b, N is presented in Fig. 2b CPA IR (KBr): 3288.74 (*versus*, OH), 2956.10 (*versus*, CH_3), 2925.19, 2855.17 (*versus*, CH_2), 1727.79 (*versus*, C=O), 1637.30 (*versus*, C=C), 1600.24, 1550.29 (*versus*, Ar), 1456.98 (d, C-H), 1228.36, 1188.95 cm^{-1} (*versus*, C-O); CPA + TDI IR (KBr, ν_{max}, cm^{-1}): 3318.59 (*versus*, NH), 2954.13 (*versus*, CH_3), 2276.67(*versus*, NCO), 1733.13 (*versus*, C=O), 1649.74 (*versus*, C=C), 1598.49, 1542.07 (*versus*, Ar), 1449.55 (d, C-H), 1223.90 cm^{-1} (NHCOO); N-CPA IR (KBr): 3422.00 (*versus*, NH), 2958.98 (*versus*, CH3), 2924.92, 2856.76 (*versus*, CH2), 1732.85, 1699.58 (*versus*, C=O), 1655.07 (*versus*, C=C), 1252.03 (*versus*, C-O), 1592.85, 1491.16 (*versus*, Ar), 1463.82 (d, C-H), 1398.12 cm^{-1} (*versus*, t-Bu); N IR (KBr, ν_{max}, cm^{-1}): 3527.64 (*versus*, OH), 2955.55 (*versus*, CH_3), 2865.30 (*versus*, CH_2), 1701.19 (*versus*, C=O), 1651.40 (*versus*, C=C), 1251.41 (*versus*, C-O), 1587.40, 1492.68 (*versus*, Ar), 1381.32, 1351.38 (*versus*, *t*-Bu). It is obvious that CPA + TDI shows a stretching vibration mode of NCO group at around 2277 cm^{-1}, whereas such peak is absent from the spectrum of CPA and N-CPA. It is well known that there are two NCO groups in TDI and *t*-Bu groups in 1,8-naphthalimide derivative. As shown in Fig. 2a, after the introduction of TDI onto CPA, three characteristic peaks of NHCOO appear at around 1250-1110 cm^{-1}; due to the grafting of 1,8-naphthalimide derivative, two different strong peaks of *t*-Bu appear at around 1380 cm^{-1}. All these facts reflect that the 1,8-naphthalimide derivative have already grafted on the copolymer through twice reactions of -OH and -NCO.

Molecular weight and molecular weight distribution of CPA and N-CPA: The number-average molecular weight (Mn), the weight-average molecular weight (Mw) and dispersities of the polymers were obtained by gel permeation chromatography (GPC, Agilent 1100 chromatograph) at 40 °C. THF was used as the eluent at a flow rate of 0.6 mL min^{-1} and standard PS as the reference (Table-2). The results shown that both number-average molecular weight (Mn) and weight-average molecular weight (Mw) of N-CPA were larger than that of CPA due to the grafting of 1,8-naphthalimide. So it is convinced that the 1,8-naphthalimide derivative have already been introduced on the main chain of CPA.

Glass transition temperature (T_g) of CPA and N-CPA: Glass transition temperature (T_g) was determined by DSC for CPA and N-CPA, respectively (Table-2). The samples were heated from -40 to 150 °C at a heating rate of 10 °C/min. The tests were put into effect in the nitrogen protection and a sample of 5-9 mg was used. The results indicated that T_g will go up owing to the weakened flexibility of the polymer chain after grafting of the rigid conjugated system of 1,8-naphthalimide derivative.

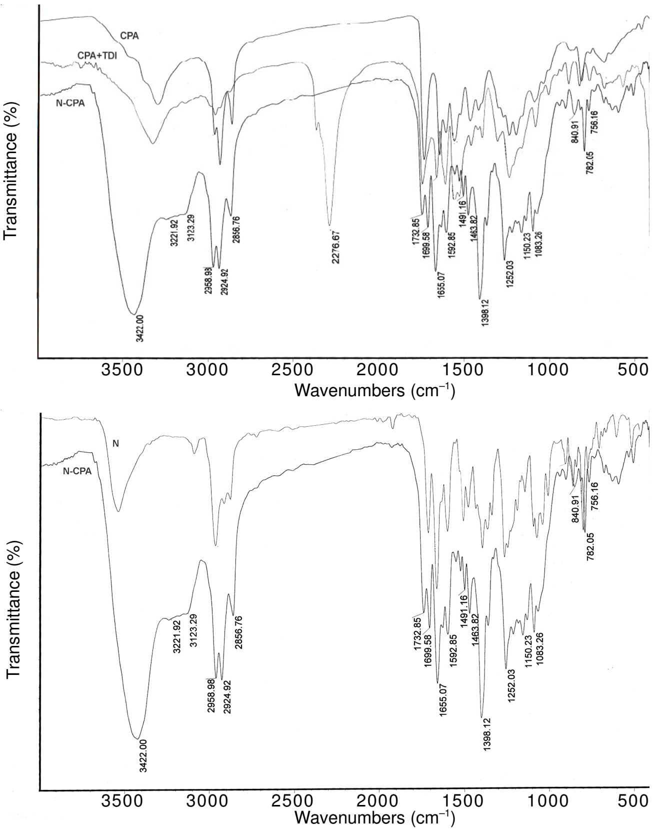

Fig. 2. (a) FTIR spectra of CPA, CPA + TDI and N-CPA. (b) FTIR spectra of N(1,8-naphthalimide) and N-CPA

TABLE-2
GPC AND DSC RESULTS OF CPA AND C-CPA

Polymer	Mn (g mol^{-1})	Mw (g mol^{-1})	D (Mw/Mn)	T_g (ºC)
CPA$_1$	6434	12323	1.92	43.0
N-CPA$_1$	8539	15523	1.82	59.3
CPA$_2$	7835	18640	2.38	54.5
N-CPA$_2$	10018	25546	2.55	76.5
CPA$_3$	9924	17788	1.79	90.7
N-CPA$_3$	14422	26579	1.84	93.7

Photoluminescence properties of 1,8-naphthalimide derivative and N-CPA: To gain blue-emitting photoluminescence polymer materials, 1,8-naphthalimide derivative was introduced into CPA. The photophysical characteristics of the target molecules are investigated in THF solutions (10^{-3} mol/L) and neat solid films as well. The data of UV-visible absorption and photoluminescence emission peaks are shown in Table-3. It can be observed that the four materials have quite similar UV-visible absorption characteristics. The maximum absorption peaks (labs), situate in 360-364 nm in solution and 368-375 nm in solid films. The data of photoluminescence emission peaks, show pure blue photoluminescence both in solution and solid films with λ PLmax locating at 445 nm around and relative narrow FWHM of 38-72 nm. But show red-shift in solid film compare to in solution. The fluorescence properties

TABLE-3
UV-VIS ABSORPTION, PHOTOLUMINESCENCE N(1,8-NAPHTHALIMIDE DERIVATIVE) AND N-CPA IN SOLUTION AND THIN SOLID FILM STATE

	In solution			In film		
	λ_{abs} (nm)	λ_{pL} (nm)	FWHM (nm)	λ_{abs} (nm)	λ_{Apex} (nm)	FWHM (nm)
N	364	444	65	375	451	72
N-CPA$_1$	362	438	40	368	441	55
N-CPA$_2$	361	438	38	369	445	50
N-CPA$_3$	360	441	50	370	455	60

in thin solid films, however, are different from those in solution be ascribed to the condensing aggregation. The results indicate the accomplishment of the purpose mentioned above.

Concentration and photoluminescence properties of N-CPA: Intrinsic relationships between concentration and photoluminescence properties of N-CPA have been investigated in detail. The fluorescence spectra of the solution of N-CPA are shown in Fig. 3. And the data of photoluminescence emission peaks are summarized in Table-4. All of the wavelengths corresponding to the maximum photoluminescence intensity of N-CPA1 locate at 437 nm around. In Table-4, when the concentration of N-CPA1 increases from 4.48×10^{-6} to 2.69×10^{-5} mol/L, the fluorescence intensity increases, but when the concentration is larger than 2.69×10^{-5} mol/L, the intensity dops. This is attributed to the reason for fluorescence quenching mechanism. Possibly, when the concentration reaches to 3.58×10^{-5} mol/L, the amount of the 1,8-naphthalimide derivative containing in N-CPA1 are too high that fluorescence intensity drops instead. To testify this phenomenon, the polymer main chain structure was changed, that is, N-CPA$_2$ and N-CPA$_3$ were synthesized corresponding to 18 and 25 % of HEA added as starting material. The results of control experiments show that as the concentration of N-CPA$_2$ and N-CPA$_3$ increases from 4.48×10^{-6} to 1.34×10^{-5} and 4.48×10^{-6} to 6.73×10^{-6} mol/L, respectively. The fluorescence intensity is increasing, then when the concentration increases further, the fluorescence intensity decreases instead (Table-4). The details suggest that the fluorescence quenching is advanced in comparison with N-CPA$_1$ due to the more amount of 1,8-naphthalimide derivative in N-CPA as the content of HEA changed from 10-18 % even 25 %. It is consistent with the conclusion is given in Fig. 4. The wavelengths corresponding to the maximum photoluminescence intensity of N-CPA$_2$ and N-CPA$_3$ also locate at 437 nm around, which signifies that the amount of the 1,8-naphthalimide containing in the N-CPA are nearly irrelevant with the wavelength corresponding to the maximum photoluminescence intensity.

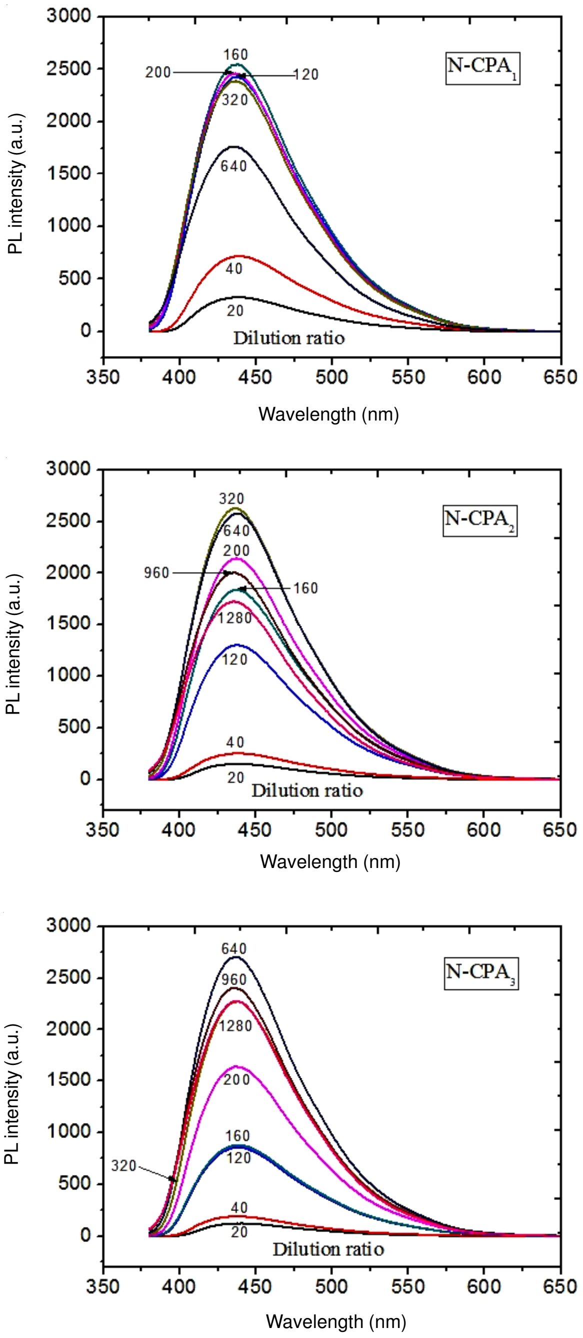

Fig. 3. Photoluminescence spectra of N-CPA in THF solution

TABLE-4
PHOTOLUMINESCENCE OF N-CPA IN THF SOLUTION

Diluti-on ratio	Concentration ($\times 10^{-6}$ mol/L)	N-CPA$_1$			N-CPA$_2$			N-CPA$_3$		
		λ_{Apex} (nm)	PL (a.u.)	FW HM (nm)	λ_{Apex} (nm)	PL (a.u.)	FW HM (nm)	λ_{Apex} (nm)	PL (a.u.)	FW HM (nm)
1280	4.48	435	1354	42	435	2008	42	435	2408	41
960	6.73	435	1766	42	438	2579	41	436	2710	40
640	13.4	436	2393	41	436	2634	41	438	2275	41
320	21.5	436	2466	41	437	2146	41	438	1643	41
200	26.9	437	2550	40	438	1841	40	440	881	41
160	35.8	437	2429	41	438	1301	41	439	860	41
40	108	439	720	41	438	253	39	437	191	37
20	2150	438	329	40	438	152	38	441	124	50

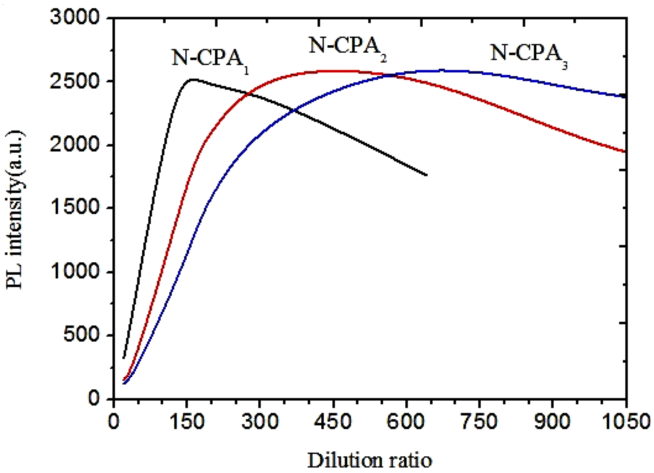

Fig. 4. Maximum photoluminescence intensity of N-CPA

Conclusion

Different proportion of HEA in the novel luminescent polymers (N-CPA) were synthesized by grafting the modified 1,8-naphthalimide derivative compound on CPA. The fluorescence spectra proved that 1,8-naphthalimide derivative and N-CPA were blue-emitting materials and the fluorescence quenching would appear when the concentration of N-CPA increased to a certain degree and the fluorescence quenching was advanced with the proportion of 1,8-naphthalimide derivative increasing. With the deepening of the research, fluorescence polymer will play a huge role in various fields of life science, environment, medicine and material due to well film-forming characteristic and optical properties.

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