Polymer Dots

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Non-Conjugated Polymer Dots with Crosslink-Enhanced Emission in the Absence of Fluorophore Units

*Shoujun Zhu, Yubin Song, Jieren Shao, Xiaohuan Zhao, and Bai Yang**

carbon nanodots · crosslink-enhanced emission · non-conjugated polymer dots · photoluminescence · sub-fluorophores

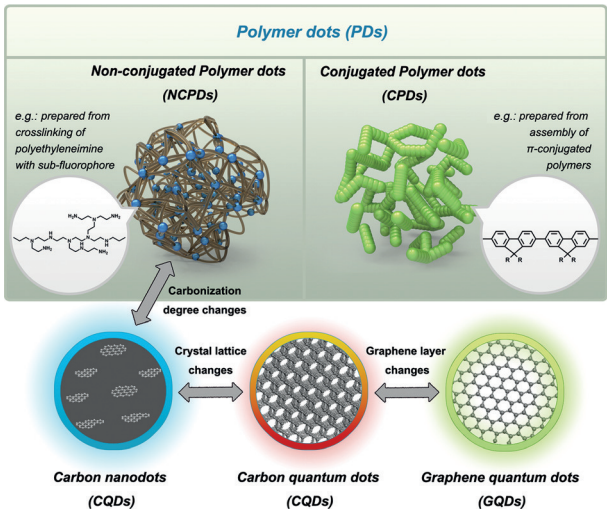
A new type of fluorescent material is presented, which is called non-conjugated polymer dots (NCPDs). The NCPDs only possess sub-fluorophores (which are groups such as C=O, C=N, N=O) instead of typical conjugated fluorophore groups, and thus these materials should not have strong photoluminescence (PL) in the usual sense. Nevertheless, the PL of these sub-fluorophores can be enhanced by chemical crosslinking or physical immobilization of polymer chains, which is named the crosslink-enhanced emission (CEE) effect. The significant advances achieved by us and other groups on both experimental and theoretical aspects are discussed, and the covalent-bond CEE, rigidity-aggregated CEE, or supramolecular CEE in NCPDs is elaborated. Moreover, synthetic strategies, unique optical properties, and the promise of NCPDs in bio-related fields, such as bioimaging and drug delivery, are systematically discussed.

1. Introduction

Polymer dots (PDs) can be divided into two subcategories: conjugated PDs (CPDs) and non-conjugated PDs (NCPDs). CPDs are produced by assembly of conjugated polymers,[1] while NCPDs, which are discussed herein, possess aggregated non-conjugated polymer structures. NCPDs are typically prepared from the non-conjugated polymers or small molecules by polymerization and crosslinking, hydrothermal treatment, self-assembly, and also physical methods. The NCPDs do not possess typical fluorophores, so the PL centers were rarely discussed. However, owing to their special polymer structures and bright fluorescence, NCPDs are very promising as novel fluorescent materials.

[*] Dr. S. Zhu, Y. Song, J. Shao, X. Zhao, Prof. B. Yang
State Key Laboratory of Supramolecular Structure and Materials
College of Chemistry, Jilin University
Changchun, 130012 (P. R. China)
E-mail: byangchem@jlu.edu.cn
Dr. S. Zhu
Department of Chemistry, Stanford University
Stanford, California 94305 (USA)

In fact, in the field of the carbon dot (CD) research, apart from graphene quantum dots (GQDs) and carbon nanodots (CNDs), NCPDs are the CDs of greatest interest (Scheme 1).[2,3] Generally, the CNDs are always spherical and they are divided into carbon nanoparticles without a crystal lattice and carbon quantum dots (CQDs) with obvious crystal lattices.[4,5] The NCPDs possess aggregated or crosslinked polymer structure



Scheme 1. Representation of PDs (the PDs always contain CPDs and NCPDs), and the relationship between NCPDs and other CDs.

without carbon structure. As a result, NCPDs are always confused with CNDs,[6–9] and some of the CNDs with "amorphous carbon" are actually NCPDs.

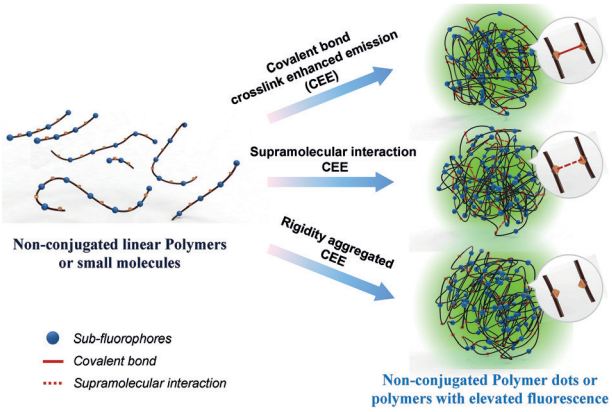
The NCPDs are a kind of fluorescent organic material, and the fluorescent organic materials also include organic dyes, conjugated polymers, as well as carbon-based materials. Among these fluorescent materials, carbon–carbon double/triple bonds or carbon-based π electrons are regarded as the main building unit for the PL center. However, some other chemical groups with weak fluorescence (we name these kinds of potential PL groups as sub-fluorophores), such as heteroatom-containing double bonds (C=O, C=N, N=O) and single bonds (amino-based groups, C–O), can show increased PL with suitable immobilization.

The immobilization methods for enhancing the PL of these materials can be covalent/supramolecular crosslinks or even physical aggregation.[10] A well-known example is poly(amidoamine) (PAMAM), in which it is generally accepted that the tertiary amine functionality is responsible for its PL center. In this system, promoting the polymer generation or decreasing the solution pH will lead to stronger emission owing to the creation of a more rigid environment, which prevents the excitons to relax through nonradiative pathways.[11] The other system that has been focused on is the purely oxygenic linear polymer, poly[(maleic anhydride)-*alt*-(vinyl acetate)]. It is indicated that PL emission of the polymer is associated with the clustering of the locked carbonyl groups.[12] These NCPDs will be used as the model systems to summarize these special PL centers and their enhancement mechanism.

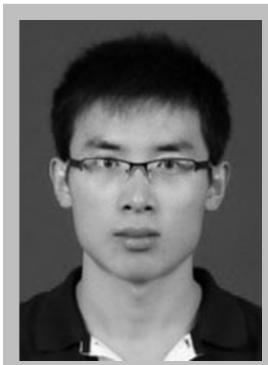
In this Minireview, we mainly focus on the synthesis and PL mechanism of NCPDs as well as their applications which utilize fluorescent properties. In Section 2, we summarize the chemical structures and synthetic routes of the NCPDs. In Section 3, we review the physical and chemical properties of the NCPDs. In Section 4, the PL mechanism on NCPDs is discussed in detail: covalent-bond crosslink-enhanced emission (CEE), rigidity-aggregated CEE, and supramolecular CEE; furthermore, this section also discusses the differences between polymer-like carbon nanodots and NCPDs and also the CEE effect in these carbon nanodots. Section 5 covers the applications of NCPDs in bioimaging, drug/gene delivery, and other fields. In Section 6, we discuss some critical issues of NCPDs awaiting further explorations. Furthermore, we investigate NCPDs as a simple model system for understanding the properties and PL-enhanced mechanism in all kinds of sub-fluorophores. We hope this Minireview can inspire more and more researchers who study the origins of these unique properties and the PL mechanisms of NCPDs. Beyond that, we expect to further expand their boundaries of applications.

2. Routes to Synthesize NCPDs

NCPDs are typically prepared from non-conjugated polymers or small molecules. According to the interaction type, non-conjugated polymer dots can be classified into three major types (Scheme 2). One is covalently crosslinked NCPDs, which have strong and directional covalent interactions between the molecular building blocks. The other two types are non-covalent NCPDs, which are formed through non-covalent interactions, and physical aggregation. The NCPDs possess different sub-fluorophores, and these sub-fluorophores exist in the backbone or side chain of the linear



Scheme 2. Representation of the covalent-bond, supramolecular-interaction, or/and rigidity-aggregated crosslink-enhanced emission (CEE) effect in non-conjugated polymer dots or polymers. The sub-fluorophores could be in the backbone or side chain of the linear non-conjugated chains; the interaction points of covalent bond or supramolecular bond could also be the sub-fluorophores themselves.



Shoujun Zhu is a postdoctoral researcher in the State Key Lab of Supramolecular Structure and Materials, Jilin University, and the Department of Chemistry, Stanford University. He received his Ph.D in polymer physics and chemistry in 2014 under the supervision of Prof. Bai Yang and Junhu Zhang at Jilin University. His research is centered on synthesis, photoluminescence mechanisms, and applications of fluorescent carbon materials containing graphene quantum dots, carbon nanodots, and polymer dots.

Bai Yang is a professor at the State Key Lab of Supramolecular Structure and Materials, College of Chemistry, Jilin University. He has authored more than 430 publications (with 11500 citations before 2015). His research was awarded the Second Prize of the State Natural Science Award of China. His current research interests are focused on polymeric carbon nanodots, polymeric nanohybridization and photoelectric materials/devices via aqueous approaches, high-performance polymeric hybrid optical materials and ordered fabrication of polymeric microstructures with multi-scale and photonic responsive materials.

Table 1: Reports of possible enhanced PL in NCPDs and linear non-conjugated polymers.

Reference[a]	Synthetic method(s)	Starting materials	Size [nm]	QY [%]	PL color	Sub-fluorophore	Possible PL mechanism[c]
[13–15]	hydrothermal and crosslinking	phenol and hexamethylenetetramine	>100	4.3	blue	phenolic hydroxy	SIE
[16][b]	polycondensation	citric acid, aliphatic diols, and various amino acids	bulk or 80	62.33	blue	N- or O-based groups	CBIE
[17]	hydrothermal	chitosan	4–7	43	blue	N- or O-based groups	CBIE
[18]	hydrothermal	grass	2–3, 18–22	2.5–6.2	blue	N- or O-based groups	CBIE
[19]	polycondensation	ethylenediamine and CCl_4	3–7	17.3	blue	amino	CBIE
[20]	hydrothermal	Linear polymer, such as PVA, PEI, polysaccharides, cellulose, and starch	2.7	1.26	blue	O-based groups	CBIE
[21][b]	polymerization	tris(2-mercaptoethyl)amine and ethylene glycol diacrylate	bulk	11–43	blue	tertiary aliphatic amines	CBIE
[22]	hydrothermal	poly(acrylamide)	5, 20, 50	12.4–12.7	blue	N- or O-based groups	CBIE
[23]	hydrothermal	glucose and glycine	1–4	<13.8	blue	N- or O-based groups	CBIE
[24]	hydrothermal	cocoon silk	70	38	blue	N- or O-based groups	CBIE
[25]	self-assembly	PEI–polylactide (PLA) copolymer	50	31	blue	amino	RAE
[26]	self-assembly	DNA	12	3.56	blue	N- or O-based groups	RAE
[10]	crosslinking, immobilization	PEI	63	0.5, 2.7, 3.2, 9.6	blue	amino	CBIE/RAE
[27]	self-assembly and crosslinking	polyethylene glycol (PEG), 2-mercaptoethylamine (MEA)-grafted poly(L-aspartic acid) (PAsp(MEA)), and PEI	ca. 100	–	blue	N- or O-based groups	RAE
[28][b]	oxidation and polymerization	N-vinyl-2-pyrrolidone, poly(N-vinylpyrrolidone)	bulk	–	blue	secondary amine oxide	CBIE
[12][b]	polymerization	maleic anhydride and vinyl acetate	bulk	20	blue	O-based groups	SIE

[a] Listed chronologically based on the received date. [b] Related to linear non-conjugated polymers. [c] SIE = supramolecular interaction enhancement, CBIE = covalent bond interaction enhancement, RAE = rigidity-aggregated enhancement.

non-conjugated chains. Owing to the crosslink or physical immobilization of the polymer chain, the sub-fluorophores possess increased photoluminescence by the CEE effect. Table 1 listed typical reported NCPDs and linear non-conjugated polymers with different synthetic methods, starting materials, potential sub-fluorophores, and possible PL mechanism.

Herein, we mainly focus on the NCPDs (but not the linear non-conjugated polymers), and discuss their synthesis methods. Methods to synthesize the NCPDs include polymerization and crosslinking, hydrothermal treatment, self-assembly, and physical methods. All of the synthesis routes have a common feature in that through them, the free and loose polymer chains with sub-fluorophores are immobilized.

2.1. Polymerization and Crosslinking

NCPDs can be synthesized by polymerizing small molecules with multiple active groups. Dai and co-workers reported the preparation of NCPDs using ethylenediamine and carbon tetrachloride (CTC) polycondensation (Figure 1a).[19] They developed an effective "ship-in-a-bottle" strategy to prepare NCPDs: use small precursor molecules to polymerize a big molecular product inside a porous matrix (for example, a microporous zeolite); the resulting product will be entrapped inside the porous matrix because of its large molecular size. The sub-fluorophore in this case is amino-based groups, which are confined by CTC crosslinking.

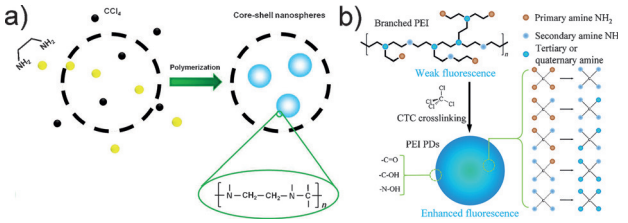


Figure 1. a) Procedure for the preparation of NCPDs. Reprinted from Ref. [19]. b) Crosslinking the branched PEI by CCl_4 (CTC). The PEI used contains 25% primary amine, 50% secondary amine, and 25% tertiary amine. Reprinted with permission from Ref. [10], copyright 2014 Royal Society of Chemistry.

Crosslinking of the linear polymer is the most direct approach to prepare NCPDs. Yu and co-workers investigated fluorescent nanospheres from crosslinked phenol formaldehyde resin.[13–15] The prepared microspheres were about 350 nm in size and are comprised of crosslinked formaldehyde and phenol. Yang and co-workers has used branched polyethyleneimine (PEI) as a model system. The NCPDs were synthesized by CTC crosslinking.[10] The initial PEI possessed very weak fluorescence. After CTC crosslinking, the NCPDs possessed increased PL (Figure 1b). In these two cases, the

potential sub-fluorophores (amino and phenol) were immobilized by the crosslinked polymer cluster and possessed increased PL properties.

Through controllable polymerization or crosslinking, NCPDs could be obtained with tunable size and crosslinking degree. It is of importance to investigate the CEE effect using adjustable NCPDs. However, it appears that there have been no publications to date on this point.

2.2. Hydrothermal Treatment

Hydrothermal treatment is a popular way to obtain nanoparticles from organic precursors. Certain molecules or polymers can form NCPDs after hydrothermal treatment. For example, Sun and co-workers reported polymer nanodots by hydrothermal treatment of grass, and the increasing reaction temperature from 150 to 200 °C leads to a decrease in size from 22 to 2 nm and an increase in QY from 2.5 to 6.2 %.[18] Yang and co-workers explored new NCPDs that were obtained from non-conjugated polymers using a one-step hydrothermal method.[20] The hydrothermal treatment can partially crosslink the polyvinyl alcohol (PVA) to form the crosslinked dots, holding the PVA chains synchronously (Figure 2); during this process, the oxygen-based sub-fluorophore was confined. Several groups reported the similar

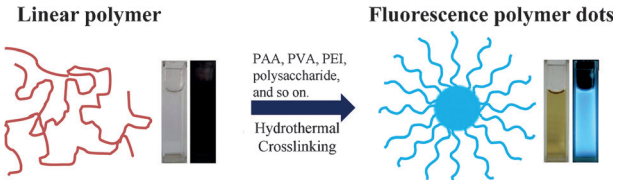


Figure 2. Photoluminescent NCPDs prepared by moderately hydrothermally treating linear polymer, such as polyvinyl alcohol (PVA). Reprinted with permission from Ref. [20], copyright 2012 Royal Society of Chemistry.

hydrothermal treatment of nature materials, such as cocoon silk,[24] glucose and glycine,[23] chitosan,[17] and they could prepare water-soluble, nitrogen-doped, photoluminescent NCPDs in water. During these processes, the amino acid and saccharide molecules can undergo dehydration to form the aggregated structures; the protein first experiences a top-down hydrolysis/degradation process to form amino acids, which then undergo a bottom-up dehydration and polymerization to produce the NCPDs. Abundant sub-fluorophore (such as amine, amide, conjugated ring in an amino acid) can be found in these biomaterials. Although hydrothermal treatment is effective and convenient, the formation process and the precise chemical structure of the product are almost impossible to establish and are uncontrollable.

2.3. Self-Assembly

The NCPDs can be prepared by the self-assembly of special polymers or biomacromolecules through supramolecular interactions. Sun et al. reported the ultrabright NCPDs (QY = 31 %) by self-assembling an amphiphilic copolymer.[25] The copolymer was based on hydrophilic PEI and hydrophobic polylactide (PLA), and drugs can also be easily encapsulated into the NCPDs through a modified emulsion/evaporation method (Figure 3 a). The enhanced fluorescence of the PEI-PLA nanoparticle and PEI-PLA copolymer powder demonstrate that the rigid and compact structure of the NCPDs plays a crucial role in fixing the sub-fluorophore and enhancing the fluorescence behavior. Guo et al. reported a new class of fluorescent bio-dots that were derived from DNA by self-assembly at low temperature (Figure 3 b).[26] The bio-dots possessed an aggregated DNA structure with a quantum yield as high as 3.65 %. Recently, Shuai and co-workers reported a very interesting dual-sensitive polymeric vector for long-circulating and tumor-targeted siRNA delivery.[27] The triblock copolymer, PEG-PAsp(MEA)-PEI, composed from polyethylene glycol (PEG), 2-mercaptoethylamine (MEA)-grafted poly(L-aspartic acid) (PAsp(MEA)), and PEI, was used to form the NCPDs by complexation and interlayer crosslinking with siRNA. The special feature of the self-assembly route to NCPDs is the use of supramolecular assembly, during which the polymer chains with sub-fluorophores are immobilized by these weak chemical bonds.

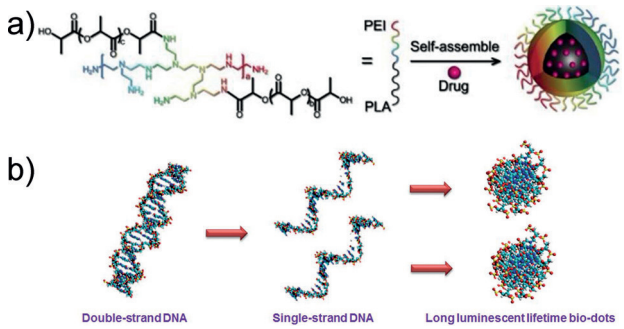


Figure 3. a) Illustration of the construction of multifunctional NCPDs from hydrophilic PEI and hydrophobic PLA amphiphilic copolymer. Reprinted with permission from Ref. [25], copyright 2013 Nature Publishing Group. b) The formation process of bio-dots. Reprinted with permission from Ref. [26], copyright 2013 Nature Publishing Group.

2.4. Physical Immobilization Routes

The sub-fluorophore on a linear polymer can also be enhanced by the chemical immobilization or just by physical aggregation. Yang and co-workers fixed the branched PEI on the surface of the carbon nanodots, and they found that the PL of the prepared NCPDs was enhanced.[10]

There were also special NCPDs which are prepared from the assembly of polymer surfactant and aggregation-induced emission (AIE) molecules or fused ring compounds.[29–31] These kinds of NCPDs are not the main subject of this Minireview, but they could be regarded as special kinds of non-conjugated polymer dots.

Although there has been few attempts to exclusively investigate the physical immobilization route to NCPDs, it

nevertheless exists in many cases. For example, both physical immobilization and supramolecular interactions can be found in living proteins, which always possess background fluorescence because of the possible sub-fluorophore and CEE behavior. Therefore, the use of these two approaches is very promising to prepare NCPDs with reversible chemical structure and PL properties.

3. Physical and Chemical Properties of NCPDs

3.1. Optical Properties

As mentioned in Section 2, there are different types of fluorescent NCPDs and various synthesis routes to obtain these materials. As a result, the chemical structures of the NCPDs are diverse in form as a consequence of the different synthesis approaches. Nonetheless, the NCPDs possess some similar optical properties regarding absorption and fluorescence. Herein we will summarize the common optical properties rather than elucidate some specific examples. The absorption of the NCPDs typically shows strong optical absorption in the UV region (230–320 nm), with a tail extending to the visible range (Figure 4).[10] The maximum

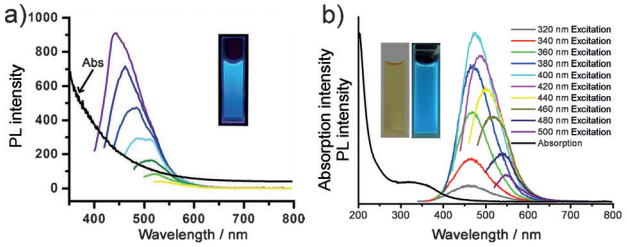


Figure 4. Fluorescence and absorption spectra of NCPDs. a) The NCPDs from ethylenediamine and CTC crosslink (excitation wavelengths from 380 nm to 500 nm in 20 nm increments). Reprinted from Ref. [19]. b) NCPDs from PEI and CTC crosslinking. The inset pictures show NCPD aqueous solutions under daylight (yellow) and UV light excitation (blue). Reprinted with permission from Ref. [10], copyright 2014 Royal Society of Chemistry.

peak in the UV region may be ascribed to an n–π* transition of C=O bonds or other sub-fluorophore groups. Furthermore, the connected chemical groups may contribute to the absorption in the UV/Vis range. The observed deviations in absorption spectra data, at least to some extent, indicate the differences of compositions or structures in different hybridization derivatives.

The PL properties are the issue of most concern for NCPDs in the view of investigation of the PL mechanism and novel applications. The synthesized NCPDs always show strong fluorescence, and there are many possibilities to affect the emission (increase or decrease the emission). The most important point is the crosslinking or immobilization of the potential sub-fluorophores. Generally, the emission peak of NCPDs is usually wide, with a large Stokes shift when compared with that of organic dyes. The emission peak position is always related to the excitation wavelength, which is called excitation-wavelength-dependent (λ_{ex}-dependent) behavior (Figure 4). It may result from the wide distribution of PL centers.

3.2. Solubility and Stability

The NCPDs always possess high physiological solubility (over 20 mg mL^{-1}) in aqueous solution.[20] It is a well-known fact that water plays the vital role in maintaining life and health, and also affords an absolutely necessary medium for a wide range of biochemical reactions and biological processes in various living organisms, and an appropriate pH range is very important.[32] In nature, there are a large number of aqueous compatible nanostructures derived from the self-assembly of natural small molecules in an aqueous medium.[33] The NCPDs show water compatible ability and good monodispersible ability in water, since the building blocks are always the hydrophilic molecules or conventional amphiphiles. The fluorescence of the NCPDs always possesses highly stability towards pH, ionic strength, and UV exposure.[19,20,26,27]

External vehicles without biodegradable or metabolizable properties will accumulate in organisms, which would be detrimental to the human body, and thus there is an urgent need to prepare and improve physiologically friendly biomedical vehicles.[37] Compared with other carbon-based materials, non-conjugated NCPDs could be spontaneously degraded or metabolized in the variable physiological environment of the human body as a result of their non-conjugated structure with dynamic/reversible non-covalent connections in the polymer backbone, displaying prominent biodegradability and biocompatibility. Therefore, the design of NCPDs with defined structure, controlled degradation profiles, and excellent biocompatibility, have great potential as a candidate for in vivo drug/gene/protein delivery systems, bioimaging agents, scaffolds for tissue engineering, and biomimetic materials.

3.3. Biocompatibility and Toxicity

The reported NCPDs always possess good biocompatibility and low toxicity.[10,16,20,25–27] In the work of Zhu et al., in vitro cytotoxicity of different NCPDs contents was evaluated with differentiated rat adrenal pheochromocytoma (PC12) cells by methylthiazolyldiphenyltetrazolium bromide (MTT) assay.[10] Experimental results suggested that NCPDs had a relative low toxicity to PC12 cells, showing relative cell viability higher than 80% with 20–30 μg mL^{-1} of NCPDs added (Figure 5a). The toxicity of the NCPDs was also tested in HeLa and 293T cells, and the result showed that the cell viabilities of both cell types declined by less than 10% upon addition of the NCPDs at up to 80 mg mL^{-1}.[24]

In the work of Sun et al., the biocompatibilities of NCPDs were investigated using a CCK-8 assay in human breast cancer MCF-7 cells (Figure 5b). The results showed that the NCPDs were much less cytotoxic than the initial PEI. The

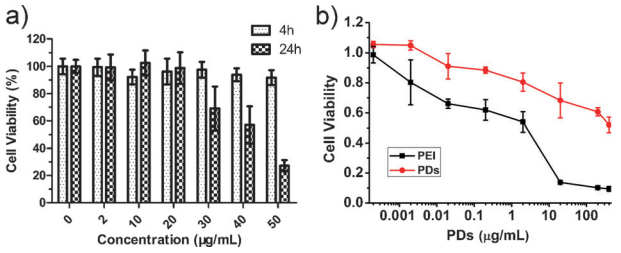


Figure 5. Cytotoxicity of NCPDs. a) Cytotoxicity of the NCPDs from PEI and CTC crosslinking. Reprinted with permission from Ref. [10], copyright 2014 Royal Society of Chemistry. b) Cytotoxicity of bare PEI and NCPDs from PEI-PLA copolymer. Reprinted with permission from Ref. [25], copyright 2013 Nature Publishing Group.

cytotoxicity of the PDs increased slightly with increasing dose concentration, but the concentrations of NCPDs used in the in vitro evaluations were significantly higher than those required for applications.[25] Furthermore, through a blood compatibility test, no hemolysis of red blood cells was caused by the NCPDs, even at a concentration of 4000 mg mL^{-1}, indicating favorable blood compatibility.

4. PL Mechanism in NCPDs

The sub-fluorophore-based chemical groups in linear polymers or polymer dots, such as heteroatom-containing double bonds (C=O, C=N, N=O) and single bonds (amino based groups, C−O), can possess increased PL with suitable immobilization. The efficient immobilization route consisted of covalent-bond CEE, supramolecular-interaction CEE, and rigidity-aggregated CEE. It should be noted that the suggested CEE was different from the reported aggregation-induced emission (AIE),[34,35] which mainly emerged in small organic molecules.

There are three key points to understand the PL mechanism of the NCPDs. First, the sub-fluorophore in the NCPDs or linear polymers is only a potential fluorophore with intrinsically very weak PL. Fortunately, the fluorescence of these sub-fluorophores can be enhanced by immobilizing (chemical crosslinking or physical aggregation). In this process, the vibration and rotation of the sub-fluorophore were restricted, leading to an increase of radiative transition. Secondly, the PL of the NCPDs was mainly controlled by the immobilized sub-fluorophores, which possess a very wide band gap.[36] As a result, the NCPDs always possess blue emission. The red-shift of the emission of NCPDs could be achieved by increasing the density of hybrid electron of the sub-fluorophore, energy transfer, and accumulated emission, as well as finding new sub-fluorophore with a narrow band gap. Finally, the NCPDs always possess λ_{ex}-dependent PL, which indicates that there are multiple excited states. Because each one of the NCPD nanoparticles is composed of plentiful sub-fluorophores, the NCPDs have a wide composition distribution, and every sub-fluorophore may be in different chemical environments, diverse PL states in the NCPDs may exist.

If we want to further understand the PL mechanism of the NCPDs, investigations on the photophysical process and theoretical calculations on the excited electron behavior are highly necessary. For example, the excited electron in the sub-fluorophore may be very different in the free polymer chains and in the confined NCPDs. Unfortunately, because research into NCPDs remains in its infancy, there are very few reports concerning on these points.

4.1. Covalent-Bond CEE

The PL mechanism of NCPDs was first confirmed to be the CEE effect by Yang and co-workers.[10] The PL properties of the potential fluorescent centers (sub-fluorophore) were amplified by the CEE effect. Using branched PEI as a model non-conjugated polymer, the CEE was investigated by PEI NCPDs. The PEI possessed a potential fluorophore (secondary and tertiary amine), and the enhanced PL originated from the decreased vibration and rotation in such crosslinked PEI-based NCPDs. Figure 1b and 4b shows the applied NCPDs and their PL properties. The NCPDs possessed temperature-dependent PL. Specifically, high temperatures are able to quench the PL to some degree. This behavior primarily confirmed that the crosslinked skeleton increased the radiative transition of the amine-based PL center in the NCPDs (the high temperature aggravated the vibration and rotation and increased the nonradiative process).

The photophysical process was made clear by the transient spectra (TA) of PEI and NCPDs (Figure 6a,b). For free PEI, there is not much contribution to the transient signals, while an obvious excited-state absorption appeared in the NCPDs, which indicated the enhanced PL behaviors from free PEI to PEI derived NCPDs.

The CEE behavior was also achieved by other model system, for example, the PL of PVA was enhanced by the hydrothermal crosslinking or the intercrossed "carbon nanorings" from linear PVA.[20,37] A very special case should be noted: some researchers have investigated the PL mechanism of the amine-based polymers and found the enhanced fluorescence was attributed to both the formation of the secondary amine oxide and "aggregation-induced emission effect". For example, Wang and co-workers has studied the PL behavior of poly(N-vinylpyrrolidone) (PVP).[28] They found that the initial pyrrolidone ring (for example, NMP) exhibited very weak fluorescence, but their hydrolyzates exhibited dramatically enhanced fluorescence, which is due to the formation of secondary amine oxide. Furthermore, the polymeric compound containing pendant pyrrolidone rings and its oxidized hydrolyzate exhibits much stronger fluorescence than the corresponding small molecular compounds owing to the crosslink-enhanced emission.

4.2. Rigidity-Aggregated CEE

Apart from the covalent-bond CEE in NCPDs or non-conjugated polymers, there is also the more-familiar physical aggregated CEE effect. As the non-radiative transition (such

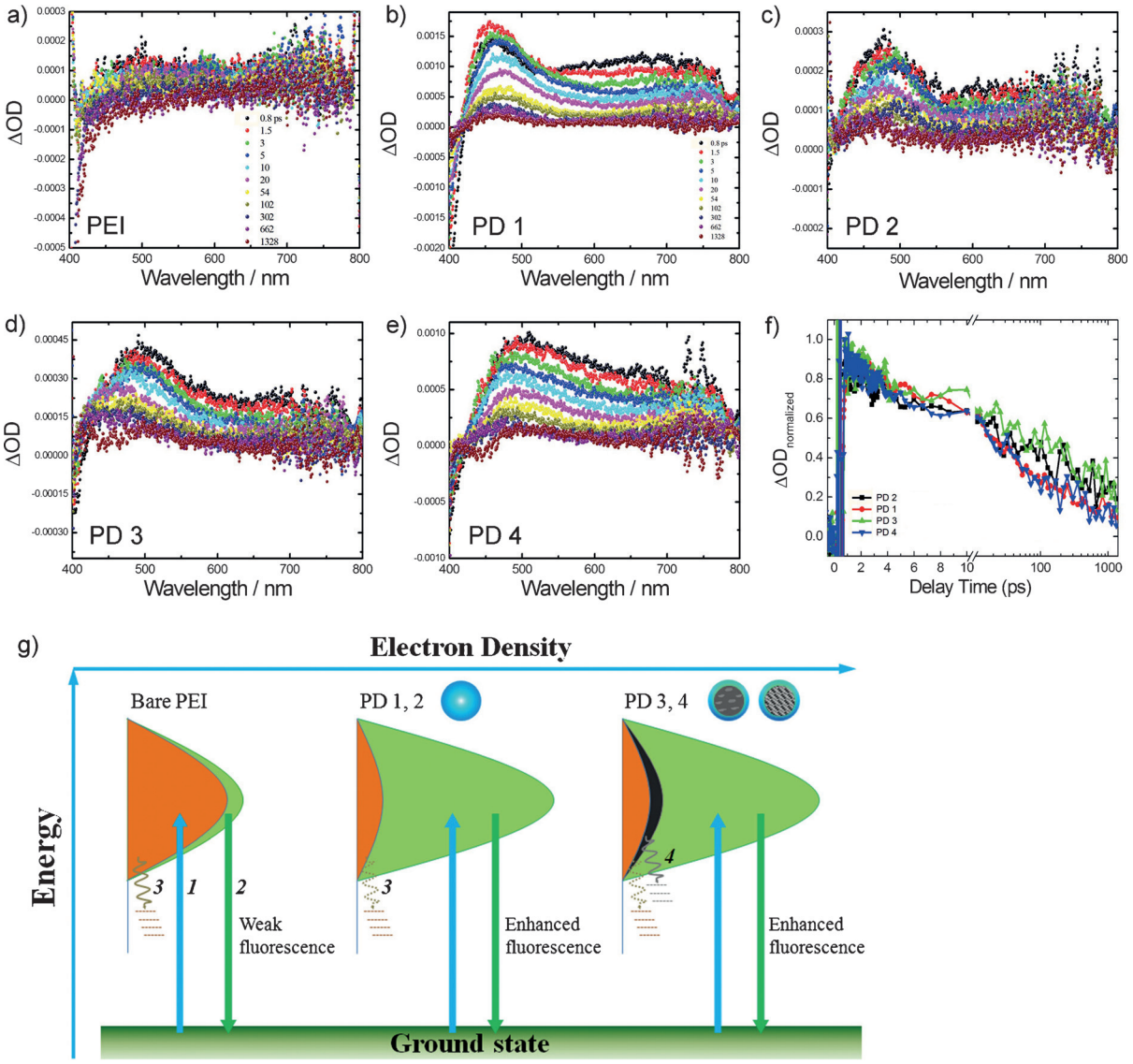


Figure 6. a–e) Transient spectra of PEI and PD 1–4. f) The normalized TA dynamics probed at 475 nm for PD 1–4. g) Representation for the PL mechanism (CEE effect) of bare PEI and PD 1–4. 1) Electrons excited from the ground state and trapped by the amino-based states; 2) excited electrons return to the ground state via a radiative route; 3) excited electrons return to the ground state via a vibrational and rotational non-radiative route; 4) excited electrons return to the ground state via a carbon core-based non-radiative route. Reprinted with permission from Ref. [10], copyright 2014 Royal Society of Chemistry.

as the vibration and rotation relaxation) can be restricted by both the chemical bond and physical confinement, the rigidity aggregation can also enhance the PL properties of the sub-fluorophore in the NCPDs.

Yang and co-workers have investigated the PL enhancement of the PEI and its fixed composites.[10] For bare PEI, the excited electrons mainly fall back to the ground state through a nonradiative vibration/rotation process. NCPD 1 and NCPD 2 were prepared by covalent-bond crosslinking and hydrothermal treatment of PEI, respectively, while NCPD 3 and NCPD 4 were obtained by immobilizing the PEI on the surfaces of the CDs with and without a crystal lattice, respectively. From TA analysis of the series of NCPDs, the similar excited-state behaviors reveal that all the NCPDs possess the same PL centers (Figure 6b–e). This is further confirmed by the same normalized TA dynamics curves with PL peaks at 475 nm (Figure 6f). For NCPDs 1 and 2, owing to the crosslinking skeleton, the vibration and rotation of the amino-based "sub-"fluorophore were restricted, and the percentage of radiative process increased (CEE effect). For NCPD 3, the PEI chains were immobilized by the amorphous carbon core, and both the immobilization of PEI chains and the antenna effect of the carbon core enhanced the PL property. For NCPD 4, although the PEI chains were fixed and the amine-based center was enhanced by the rigidity aggregated CEE effect, the carbon core with multi-layer crystal lattice possessed non-radiative structures and traps. As a result, the radiative process was neutralized and confined (Figure 6g).

Sun and co-workers reported ultrabright amphiphilic NCPDs by self-assembly of segmented copolymer.[25] They demonstrated that the rigid and compact structure of the NCPDs played a crucial role in the behavior of λ_{ex} dependence and enhancing fluorescence. The pH-dependent fluorescence of NCPDs further confirmed that the acidic environment generated a much more rigid and compact conformation and induced the unique fluorescent effect.

Dendrimers (such as PAMAMs) are a very special case of NCPDs. They generally possess a sphere-like shape, and they are typified by an internal molecular architecture consisting of tree-like branching, with each outward layer, or generation, containing many exponentially branching points.[38] Owing to steric hindrance, the sub-fluorophore is physically immobilized and thus they have enhanced PL.

It should be noted that environmental factors (such as concentration, pH) can affect the rigidity aggregation degree of the NCPDs, and further impact the PL of the NCPDs. For example, no significant emission was produced by low-molecular-weight amine samples or aqueous solutions with low concentration, whereas the opposite show enhanced PL, indicating that the high local concentration of amine groups (amine cluster) is important for the remarkable emission of polyamine polymers; this may help delocalizing of electron holes produced from amine groups in the excited state.

4.3. Supramolecular-Interaction CEE

The basic PL enhanced mechanism in the NCPDs is a decrease in the vibration and rotation of sub-fluorophore groups, increasing the radiative transition accordingly. As a result, just like the covalent-bond and the rigidity-aggregated crosslink enhanced emission, the supramolecular interaction could play a similar role in enhancing the PL emission of the sub-fluorophore.

Although there have been few reports on NCPDs with solely supramolecular-interaction CEE, it co-exists in many covalent-bond or rigidity-aggregated CEE systems. There are always hydrogen bonds and van der Waals interactions in these systems; for example, Yang et al. reported aliphatic biodegradable photoluminescent polymers (BPLPs) and their associated crosslinked variants (Figure 7).[16] BPLPs are degradable oligomers synthesized from biocompatible monomers, including citric acid, aliphatic diols, and various amino acids, by a convenient and cost-effective condensation reaction. BPLPs can be further crosslinked into elastomeric polymers. In the structure of crosslinked BPLPs, the multiple hydrogen bond also contributed to the enhanced PL besides the covalent bond CEE. Owing to diversity of the supramolecular interactions, such as hydrogen bonds, van der Waals interactions, π–π interactions, host–guest interactions, and coordination, it will be very interesting to prepare the NCPDs with these reversible supramolecular interactions that produce responsive PL behavior.

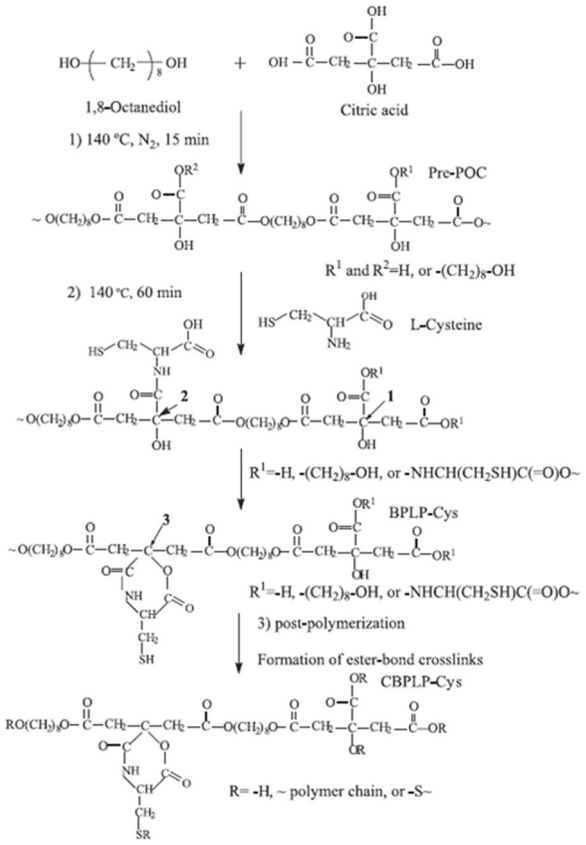


Figure 7. Synthesis of BPLPs. Reprinted with permission from Ref. [16], copyright 2009 Proceedings of the National Academy of Science of the United States of America.

4.4. The CEE Effect in Polymer-like CNDs

NCPDs are always discovered in the synthesis of bottom-up carbon nanodots, and many of the reported carbon nanodots were very similar to these NCPDs.[2] It is confusing to distinguish the concept between NCPDs and CNDs, and especially the polymer-like CNDs. We suggested distinguishing them according to chemical structure and PL mechanism. For CNDs, surface groups and the carbon core are both important to the PL. For NCPDs, the degree of carbonization is very low (or there is no carbonization) and the polymer chain structure is preserved, and the PL derives from the CEE effect of the sub-fluorophores.

Some reported CNDs prepared from small-molecule precursors may be NCPDs in some sense (polymer-like CNDs), since the starting materials are polymerized in the synthetic process. For example, Lai et al. reported a type of NCPDs from hydrothermal treatment of glucose and glycine.[23] Shi et al. synthesized CNDs using ethylenediaminetetraacetic acid (EDTA) as a precursor.[39] However, some PL nanoparticles from non-conjugated polymers are not typical NCPDs. The polymer depolymerized or fractured into segments in these examples, and the segments were the building block for CNDs.[40] Hu et al. developed a method to synthesize CNDs by hydrothermal treatment of various waste plastic bags in low-concentration H_2O_2 solutions.[41] The polyethy-

lene chain of the waste plastic bags was firstly cut into small oxidized species. Then these species undergo polymerization, carbonization, and passivation to produce CNDs. In other examples, NCPDs further carbonize to form CNDs through heating. In fact, crosslinked NCPDs are a common precursor of CNDs. In this aspect, it is hard to find a value to estimate the degree of carbonization for distinguishing NCPDs and CNDs.

The CEE effect may generally apply for many typical NCPDs and some types of polymer-like CNDs. For example, Yang and co-workers investigated the CNDs from citric acid and ethylenediamine.[42,43] At a reaction temperature of less than 150 °C, a kind of fluorophore with high QYs formed. At a reaction temperature from 150–300 °C, the CA and EDA formed the fluorophore molecules, crosslink polymer clusters, and also the CND core. There was a reaction equilibrium among these components (Figure 8).[44] Elevated reaction temperature lead the reaction equilibrium move to the polymer cluster or carbon core. A polymer-like structure is essential for the formation of CNDs.[45] Further investigation showed that the polymer cluster is one product in the CNDs and the CEE effect may contribute to the synergistic PL in polymer clusters (Figure 8b).[44,45]

Furthermore, even if observed in a few typical NCPDs, CEE may not be the reason for PL. In some situations, polymerization or crosslinking is not effective to enhance the PL. For example, Zhang et al. synthesized CNDs and then functionalized them with glycidyl methacrylate on the surface to produce polymerizable CNDs.[46] Experimental results showed that after polymerization, neither a significant difference of the PL spectra, nor an increase of quantum yields was found. The CNDs was polymerized, but the PL center of the CNDs was not immobilized, so no PL enhancement was observed.

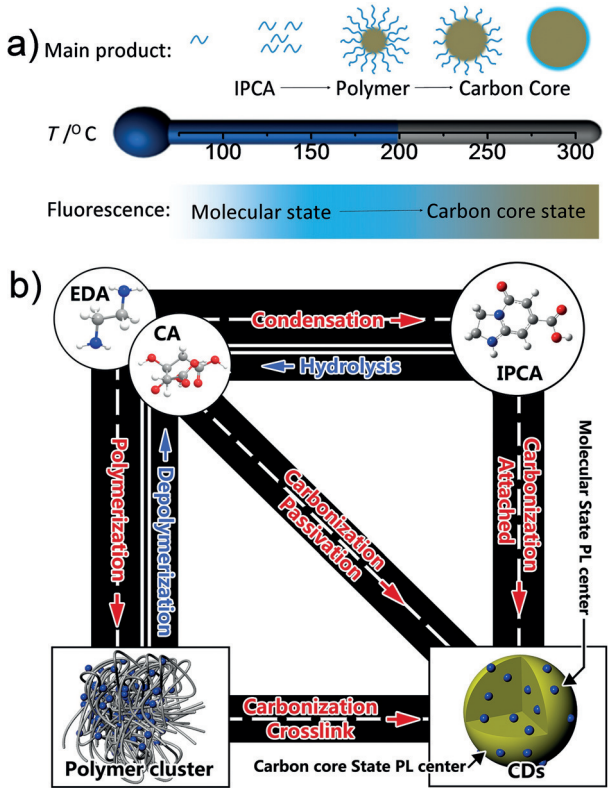


Figure 8. a) CDs obtained from different hydrothermal treatment temperatures. b) The relationship between different products in the one-pot hydrothermal system of CA and EDA. The polymer cluster was the key concern in this article. Reprinted with permission from Ref. [44], copyright 2015 Royal Society of Chemistry.

5. Biologically Based Applications of NCPDs

NCPDs possess outstanding photoluminescence, good stability, and low toxicity, which are very important for biologically based applications. Now we focus on the functional NCPDs for applications in the biomedical field, including drug delivery, gene transfection, and bioimaging. Because there are only a few reports of biological applications of NCPDs, we hope this section could serve as a brief introduction to encourage researchers to expand the applications of these novel materials.

5.1. Drug Delivery and Therapy

Drug delivery refers to technologies, approaches, and systems for delivering pharmaceutical agents into human tumor tissues to safely realize its expected therapeutic effect. Up to now, NCPDs have been used as promising drug carriers for improving the water solubility and bioavailability of drugs, inducing preferential accumulation at tumor sites, prolonging the circulation time, and reducing systemic side effects. In the work of Sun et al., PEI has been conjugated with hydrophobic polylactide to become the amphiphilic PEI for construction of NCPDs, which showed enhanced fluorescence (rigidity-aggregated CEE) with a high drug-loading capacity.[25] Paclitaxel (PTX)-loaded nanoparticles showed a significant therapeutic effect compared with free PTX. Meanwhile, fluorescence imaging of the NCPDs showed the accumulation of NCPDs around the tumor. Drug-release experiments showed that in both acidic conditions (pH 5.2) and physiological conditions (pH 7.4), there was an initial burst of PTX release from the NCPDs within the first 12 h, followed by sustained release (Figure 9). However, PTX was released much faster at pH 5.2 than that at pH 7.4, indicating that the PTX-loaded NCPDs have a pH-sensitive release profile. This pH sensitivity may benefit the release of PTX when drug-loaded NCPDs enter the acidic endosome/lysosome compartments of cells. These results demonstrate a new type of polymer-based multifunctional nanoparticles that have been prepared for imaging-guided drug delivery.

5.2. Tumor-Targeted siRNA Delivery

Gene therapy has gained enormous attention during the past two decades as a potential approach for correcting genetic disorders or silencing tumor-specific genes, which serves as an alternative strategy to the conventional chemo-

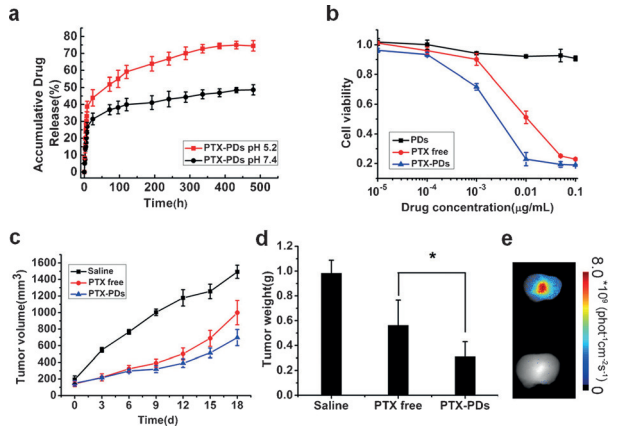


Figure 9. a) In vitro drug release of PTX-loaded NCPDs under acidic conditions (pH 5.2) and physiological conditions (pH 7.4). b) Cytotoxicity of free PTX, PTX-loaded NCPDs, and blank NCPDs after 48 h incubation with MCF-7 cells. The concentration of blank NCPDs used was equal to the concentration of PTX-loaded NCPDs. c,d) Tumor volume and tumor weight of MCF-7 tumor-bearing female nude mice treated with saline, PTX, or PTX-loaded NCPDs. e) Fluorescence images showing the ex vivo bio-distribution of NCPDs in tumors isolated from the mice that had formed after intravenous injection. Lower: saline group; Upper: PTX-loaded NCPDs group. Reprinted with permission from Ref. [25], copyright 2013 Nature Publishing Group.

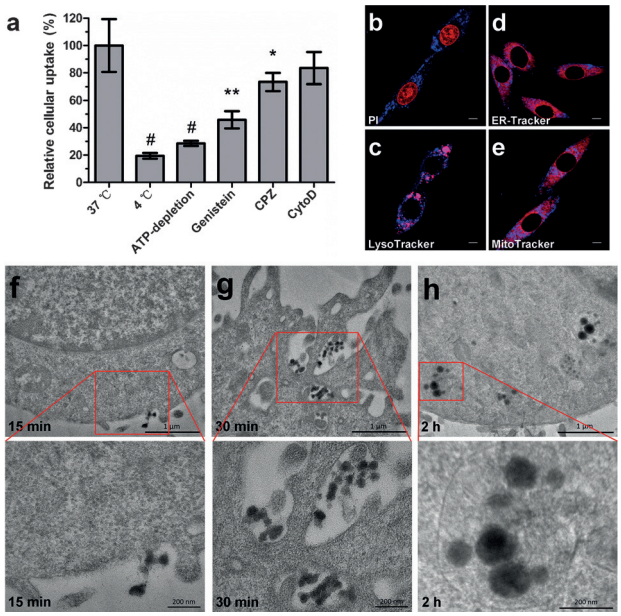


Figure 10. a) The fluorescence-activated cell sorter (FACS) quantitative data for the uptake of NCPDs by PC12 cells incubated at 37 °C, 4 °C, ATP-depletion, inhibitors Genistein, chlorpromazine, and cyto D treatments, respectively. b)–e) NCPDs co-localized with cellular organelle specific dyes in PC12 cells. Scale bar: 5 μm. f)–h) The endocytotic process of NCPDs entering a cell was detected by fixed-slice TEM. Scale bars: 1 μm for upper images and 200 nm for lower images. Reprinted with permission from Ref. [10], copyright 2014 Royal Society of Chemistry.

therapy that is used in treating countless diseases. Gene therapy always uses non-viral vector systems, such as cationic lipids, polymers, dendrimers, and peptides; as a result, NCPDs show great promise to achieve fascinating applications with more integrations and modifications in contrast to the homogenous material. For example, a PEG–PAsp(MEA)–PEI triblock polymer has been used to deliver small interfering RNA into the tumor cells.[27] Upon forming a compact compound with these amine-contained cationic polymers, the small interfering RNA molecules can be protected from enzymatic degradation in vivo. Furthermore, the NCPDs can be readily modified with a tumor targeting ligand to enable tumor cell-specific uptake and action. And the surface charge-reversible character owing to the PEI proton-buffering effect may protect small interfering RNA from degradation and meanwhile maintain initial size stability in blood circulation.

5.3. Bioimaging

Bioimaging is an emerging research field aimed at using sophisticated bioimaging probes to visualize specific molecular pathways in vivo. Currently, the majority of bioimaging probes utilized in clinical practice are small-molecule compounds that tend to be unstable, toxic, nonspecific, and rapidly cleared. In sharp contrast, NCPD-based bioimaging probes have remarkably improved stability, reduced toxicity, prolonged plasma half-lives, enhanced emission and enhanced target specificity, and can be used as promising candidates for specifically targeted clinical bioimaging in the future.

The cellular uptake mechanism and internalization of NCPDs were investigated by Zhu et al. in detail.[10] Owing to the energy-dependent effect, the complete endocytosis of NCPDs was shown to be suppressed at low temperature or in ATP-depleted environments (Figure 10a). The endocytosis pathways of NCPDs were further investigated by the addition of pharmacological inhibitors (Figure 10a). The results confirmed that NCPDs were internalized by caveolae-, clathrin-, and macropinocytosis-mediated endocytosis in PC12 cells. The intracellular distribution of NCPDs was investigated by co-localizing with specific dyes of cell organelles in PC12 cells. Propidium iodide (PI), LysoTracker red, ER-Tracker red, and MitoTracker red were used to label nucleus, lysosomes, endoplasmic reticulum, and mitochondria, respectively. The NCPDs were shown to be mainly distributed in cytoplasm and mitochondria (Figure 10b–e). Furthermore, the intracellular distribution of NCPDs in PC12 cells was confirmed using fixed-slice TEM. As shown in Figure 10f–h, a typical endocytosis process was observed at different culture stages, and NCPDs were wrapped by the formed vacuolar in 2 h culturing.

6. Conclusions and Outlook

Currently, great progress has been made in the field of functional non-conjugated PDs. The synthesis methods, CEE mechanism, and biologically based applications were de-

scribed comprehensively. However, this area is still in its infancy, and faces several key challenges.

First, the CEE should be a fundamental scientific issue, which is very important for the fluorescence of NCPDs and some kind of CNDs. The CEE behavior is applicable to non-conjugated polymer systems with sub-fluorophores (heteroatom-containing double bonds, such as C=O, C=N, N=O, and single bonds, such as amino groups, C−O). The λ_{ex}-dependent PL of NCPDs indicated that there were multiple excited states without energy transfer between them. Owing to the large band gap of the sub-fluorophores, the NCPDs typically involve blue emission. As a result, more and more synthetic approaches should be developed to NCPDs with high quantum yield, emission in the full visible region, and reversible PL.

Second, the current functionality of the NCPDs is still relatively simple and monotonous; therefore, the design and development of multiple and sophisticated functional NCPDs has become an urgent and indispensable need. Special routes, such as crosslinking upon UV irradiation or thermal annealing, can be adopted to prepare these NCPDs. Furthermore, a large number of biodegradable, biocompatible, or bioresorbable synthetic polymers, such as polyols, polyethers, polyesters, polylactides, and polyphosphates, should be used as ideal building blocks to prepare functional NCPDs.

Third, the current knowledge is very important for understanding fluorescence behaviors in well-known linear polymers and biomacromolecules, which generally possess distinct luminesce under a certain excitation wavelengths. The reason is that the existing sub-fluorophores in these systems are crosslinked or immobilized, and give bright photoluminescence. For example, when the PVA aqueous solution was frozen to form a gel, fluorescence appeared; the protein in the living body always possesses background fluorescence because of the possible sub-fluorophore and CEE behaviors (multistage aggregation structures).

Finally, the majority of functional NCPDs have only been used for in vitro biomedical applications, and thus there is still a long way to go before they are applied to clinical diagnosis and therapy. Therefore, the relevant research in this area is still far from sufficient, and much more work needs to be done. Furthermore, the NCPDs retain the classical properties of traditional polymers, such as viscoelasticity and processibility, it will be very promising to exploit various applications based on these NCPDs.[47]

Acknowledgements

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[1] C. Wu, D. T. Chiu, *Angew. Chem. Int. Ed.* **2013**, *52*, 3086–3109; *Angew. Chem.* **2013**, *125*, 3164–3190.
[2] S. Zhu, Y. Song, X. Zhao, J. Shao, J. Zhang, B. Yang, *Nano Res.* **2015**, *8*, 355–381.
[3] a) Y. Song, S. Zhu, B. Yang, *RSC Adv.* **2014**, *4*, 27184–27200; b) S. Zhu, S. Tang, J. Zhang, B. Yang, *Chem. Commun.* **2012**, *48*, 4527–4539.
[4] L. Cao, M. J. Meziani, S. Sahu, Y. P. Sun, *Acc. Chem. Res.* **2013**, *46*, 171–180.
[5] H. Li, Z. Kang, Y. Liu, S.-T. Lee, *J. Mater. Chem.* **2012**, *22*, 24230–24253.
[6] K. Lawrence, F. Xia, R. L. Arrowsmith, H. Ge, G. W. Nelson, J. S. Foord, M. Felipe-Sotelo, N. D. Evans, J. M. Mitchels, S. E. Flower, S. W. Botchway, D. Wolverson, G. N. Aliev, T. D. James, S. I. Pascu, F. Marken, *Langmuir* **2014**, *30*, 11746–11752.
[7] E. J. Goh, K. S. Kim, Y. R. Kim, H. S. Jung, S. Beack, W. H. Kong, G. Scarcelli, S. H. Yun, S. K. Hahn, *Biomacromolecules* **2012**, *13*, 2554–2561.
[8] D. Chowdhury, N. Gogoi, G. Majumdar, *RSC Adv.* **2012**, *2*, 12156–12159.
[9] A. Sachdev, I. Matai, P. Gopinath, *RSC Adv.* **2014**, *4*, 20915–20921.
[10] S. Zhu, L. Wang, N. Zhou, X. Zhao, Y. Song, S. Maharjan, J. Zhang, L. Lu, H. Wang, B. Yang, *Chem. Commun.* **2014**, *50*, 13845–13848.
[11] W. I. Lee, Y. Bae, A. J. Bard, *J. Am. Chem. Soc.* **2004**, *126*, 8358–8359.
[12] E. Zhao, J. W. Y. Lam, L. Meng, Y. Hong, H. Deng, G. Bai, X. Huang, J. Hao, B. Z. Tang, *Macromolecules* **2015**, *48*, 64–71.
[13] S.-R. Guo, J.-Y. Gong, P. Jiang, M. Wu, Y. Lu, S.-H. Yu, *Adv. Funct. Mater.* **2008**, *18*, 872–879.
[14] P. Yang, Y. Zhao, Y. Lu, Q. Z. Xu, X. W. Xu, L. Dong, S. H. Yu, *ACS Nano* **2011**, *5*, 2147–2154.
[15] J. Zhang, Y. Yuan, Z. L. Yu, A. Yu, S. H. Yu, *Small* **2014**, *10*, 3662–3666.
[16] J. Yang, Y. Zhang, S. Gautam, L. Liu, J. Dey, W. Chen, R. P. Mason, C. A. Serrano, K. A. Schug, L. Tang, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 10086–10091.
[17] Y. Yang, J. Cui, M. Zheng, C. Hu, S. Tan, Y. Xiao, Q. Yang, Y. Liu, *Chem. Commun.* **2012**, *48*, 380–382.
[18] S. Liu, J. Tian, L. Wang, Y. Zhang, X. Qin, Y. Luo, A. M. Asiri, A. O. Al-Youbi, X. Sun, *Adv. Mater.* **2012**, *24*, 2037–2041.
[19] Z. A. Qiao, Q. Huo, M. Chi, G. M. Veith, A. J. Binder, S. Dai, *Adv. Mater.* **2012**, *24*, 6017–6021.
[20] S. Zhu, J. Zhang, L. Wang, Y. Song, G. Zhang, H. Wang, B. Yang, *Chem. Commun.* **2012**, *48*, 10889–10891.
[21] M. Sun, C. Y. Hong, C. Y. Pan, *J. Am. Chem. Soc.* **2012**, *134*, 20581–20584.
[22] J. Gu, W. Wang, Q. Zhang, Z. Meng, X. Jia, K. Xi, *RSC Adv.* **2013**, *3*, 15589–15591.
[23] T. Lai, E. Zheng, L. Chen, X. Wang, L. Kong, C. You, Y. Ruan, X. Weng, *Nanoscale* **2013**, *5*, 8015–8021.
[24] W. Li, Z. Zhang, B. Kong, S. Feng, J. Wang, L. Wang, J. Yang, F. Zhang, P. Wu, D. Zhao, *Angew. Chem. Int. Ed.* **2013**, *52*, 8151–8155; *Angew. Chem.* **2013**, *125*, 8309–8313.
[25] Y. Sun, W. Cao, S. Li, S. Jin, K. Hu, L. Hu, Y. Huang, X. Gao, Y. Wu, X. J. Liang, *Sci. Rep.* **2013**, *3*, 3036.
[26] C. X. Guo, J. Xie, B. Wang, X. Zheng, H. B. Yang, C. M. Li, *Sci. Rep.* **2013**, *3*, 2957.
[27] J. Li, X. Yu, Y. Wang, Y. Yuan, H. Xiao, D. Cheng, X. Shuai, *Adv. Mater.* **2014**, *26*, 8217–8224.
[28] G. Song, Y. Lin, Z. Zhu, H. Zheng, J. Qiao, C. He, H. Wang, *Macromol. Rapid Commun.* **2015**, *36*, 278–285.
[29] D. Ding, C. C. Goh, G. Feng, Z. Zhao, J. Liu, R. Liu, N. Tomczak, J. Geng, B. Z. Tang, L. G. Ng, B. Liu, *Adv. Mater.* **2013**, *25*, 6083–6088.

[30] S. Zhu, L. Wang, B. Li, Y. Song, X. Zhao, G. Zhang, S. Zhang, S. Lu, J. Zhang, H. Wang, H. Sun, B. Yang, *Carbon* **2014**, *77*, 462 – 472.
[31] K. Li, W. Qin, D. Ding, N. Tomczak, J. Geng, R. Liu, J. Liu, X. Zhang, H. Liu, B. Liu, B. Z. Tang, *Sci. Rep.* **2013**, *3*, 1150.
[32] J. C. Orr, V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, R. A. Feely, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, R. M. Key, K. Lindsay, E. Maier-Reimer, R. Matear, P. Monfray, A. Mouchet, R. G. Najjar, G. K. Plattner, K. B. Rodgers, C. L. Sabine, J. L. Sarmiento, R. Schlitzer, R. D. Slater, I. J. Totterdell, M. F. Weirig, Y. Yamanaka, A. Yool, *Nature* **2005**, *437*, 681 – 686.
[33] J. Roughgarden, S. Gaines, H. Possingham, *Science* **1988**, *241*, 1460 – 1466.
[34] Y. Hong, J. W. Lam, B. Z. Tang, *Chem. Commun.* **2009**, 4332 – 4353.
[35] Y. Hong, J. W. Lam, B. Z. Tang, *Chem. Soc. Rev.* **2011**, *40*, 5361 – 5388.
[36] A. B. Mabire, M. P. Robin, W. D. Quan, H. Willcock, V. G. Stavros, R. K. O'Reilly, *Chem. Commun.* **2015**, *51*, 9733 – 9736.
[37] X. Li, Y. Liu, X. Song, H. Wang, H. Gu, H. Zeng, *Angew. Chem. Int. Ed.* **2015**, *54*, 1759 – 1764; *Angew. Chem.* **2015**, *127*, 1779 – 1784.
[38] Y. Shen, X. Ma, B. Zhang, Z. Zhou, Q. Sun, E. Jin, M. Sui, J. Tang, J. Wang, M. Fan, *Chem. Eur. J.* **2011**, *17*, 5319 – 5326.
[39] Q.-Q. Shi, Y.-H. Li, Y. Xu, Y. Wang, X.-B. Yin, X.-W. He, Y.-K. Zhang, *RSC Adv.* **2014**, *4*, 1563 – 1566.
[40] M. Chen, W. Wang, X. Wu, *J. Mater. Chem. B* **2014**, *2*, 3937 – 3945.
[41] Y. Hu, J. Yang, J. Tian, L. Jia, J.-S. Yu, *Rsc Adv.* **2014**, *4*, 47169 – 47176.
[42] S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang, B. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3953 – 3957; *Angew. Chem.* **2013**, *125*, 4045 – 4049.
[43] Y. Song, S. Zhu, S. Xiang, X. Zhao, J. Zhang, H. Zhang, Y. Fu, B. Yang, *Nanoscale* **2014**, *6*, 4676 – 4682.
[44] Y. Song, S. Zhu, S. Zhang, Y. Fu, L. Wang, X. Zhao, B. Yang, *J. Mater. Chem. C* **2015**, *3*, 5976 – 5984.
[45] L. Deng, X. Wang, Y. Kuang, C. Wang, L. Luo, F. Wang, X. Sun, *Nano Res.* **2015**, *8*, 2810 – 2821.
[46] P. Zhang, W. Li, X. Zhai, C. Liu, L. Dai, W. Liu, *Chem. Commun.* **2012**, *48*, 10431 – 10433.
[47] S. Zhu, J. Zhang, Y. Song, G. Zhang, H. Zhang, B. Yang, *Acta Chim. Sin.* **2012**, *70*, 2311 – 2315.

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