

Matrix Effect on Polydiarylfluorenes Electrospun Hybrid Microfibers: From Morphology Tuning to High Explosive Detection Efficiency

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Electronic Supplementary Information

Abstract Precisely optimizing the morphology of functional hybrid polymeric systems is crucial to improve its photophysical property and further extend their optoelectronic applications. The physic-chemical property of polymeric matrix in electrospinning (ES) processing is a key factor to dominate the condensed structure of these hybrid microstructures and further improve its functionality. Herein, we set a flexible poly(ethylene oxide) (PEO) as the matrix to obtain a series of polydiarylfluorenes (including PHDPF, PODPF and PNDPF) electrospun hybrid microfibers with a robust deep-blue emission. Significantly different from the rough morphology of their poly(*N*-vinylcarbazole) (PVK) ES hybrid fibers, polydiarylfluorenes/PEO ES fibers showed a smooth morphology and small size with a diameter of 1~2 μm. Besides, there is a relatively weak phase separation under rapid solvent evaporation during the ES processing, associated with the hydrogen-bonded-assisted network of PEO in ES fibers. These relative “homogeneous” ES fibers present efficient deep-blue emission (PLQY>50%), due to weak interchain aggregation. More interestingly, low fraction of planar (β) conformation appears in the uniform PODPF/PEO ES fibers, induced by the external traction force in ES processing. Meanwhile, PNDPF/PEO ES fibers present a highest sensitivity than those of other ES fibers, associated with the smallest diameter and large surface area. Finally, compared to PODPF/PVK fibers and PODPF/PEO amorphous ES fibers, PODPF/PEO ES fibers obtained from DCE solution exhibit an excellent quenching behavior toward a saturated DNT vapor, mainly due to the synergistic effect of small size, weak separation, β -conformation formation and high deep-blue emission efficiency.

Keywords Matrix effect; Electrospun fibers; Polydiarylfluorenes; Planar conformation; Explosive detection

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INTRODUCTION

In the last decades, light-emitting π -conjugated polymers (LCPs) have attracted more and more attentions in fundamental researches and industrial areas, owing to the easily structural modification, high emission efficiency and intrinsically flexible mechanical properties.^[1–11] Up to date, *p* (D)-*n* (A) molecular design is an effective strategy to precisely tune the intramolecular π -electron delocalization and interchain π -electron coupling,^[12–15] and the former controls the absorption

and emission behavior,^[13,16] while the latter is crucial for improving the charge transport ability and exciton diffusion in solid states.^[17–21] In fact, in addition to the intrinsic electronic structure, the hierarchical structure of LCPs is the key factor in improving their photophysical properties and expanding their optoelectronic applications.^[4,22–26] For example, as a preliminary structure, chain structure is the fundamental parameter that determines electronic structure, conformational behavior and condensed structure.^[12–14,27,28] Significantly different from insulating plastics, “secondary” conformational behavior of LCPs chain can not only precisely control the effective conjugated length and electron delocalization, but also modulate interchain packing model.^[29–32] Finally, condensed structures (including interchain arrangement and surface morphology) will also dominate the excitons formation, migration and diffusion, and energy transfer, thus affecting the emission efficiency, color purify and charge mobility.^[10,25,26,33–36]

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Therefore, precisely controlling hierarchical structure of LCPs provides an effective strategy to improve their photophysical properties and expand optoelectronic applications.

Among all experimental parameters, directional force can induce chain complanation, anisotropic interchain arrangement and excellent one-dimensional nanostructure morphology of LCPs.^[17–19,37] It is a convenient means to adjust and improve the optoelectronic properties of LCPs.^[38] In general, electrospinning is a universal technique for achieving this external force to obtain one-dimensional nano- and microstructure with diverse molecular conformations and morphologies.^[39–43] In fact, the size and surface morphology of these electrospun (ES) fibers are important parameters to affect the photophysical properties and their practical applications.^[43,44] Meanwhile, the efficient dispersion of LCPs chain in hybrid electrospun fibers can also improve the emission efficiency and color purity.^[43] Beyond the preparation conditions, considering the requirement of the high viscosity of precursor solutions in electrospinning processing, the selection of polymer matrix can be used to adjust the size, component dispersion and morphology of electrospun fibers, together with the hierarchical structure (including chain conformation and interchain arrangement) of LCPs.^[43,45] As a kind of important deep-blue LCPs, polyfluorene (PFs) is used as an emissive component in ES fibers due to their high deep-blue efficiency. It has been widely applied in organic laser, organic light-emitting diodes and organic sensor.^[16,46] Therefore, according to our recent work,^[41] polydiarylflorenes (PHDPF, PODPF and PNDPF) and poly(*N*-vinylcarbazole) (PVK) hybrid ES fibers are obtained to check the effect of molecular structure on the conformational behavior (Schemes 1a and 1b). However, these hybrid ES fibers present a large size with a width of >8 μm. Meanwhile, a series of micro-aggregate are observed in these fibers. This indicates that there is severe phase separation and inefficient dispersion in ES fibers, which are negatively effect on the emission behavior for the detection sensitivity of explosives. More importantly, there are many pores found on the surface of polydiarylflorenes/PVK ES fibers, fur-

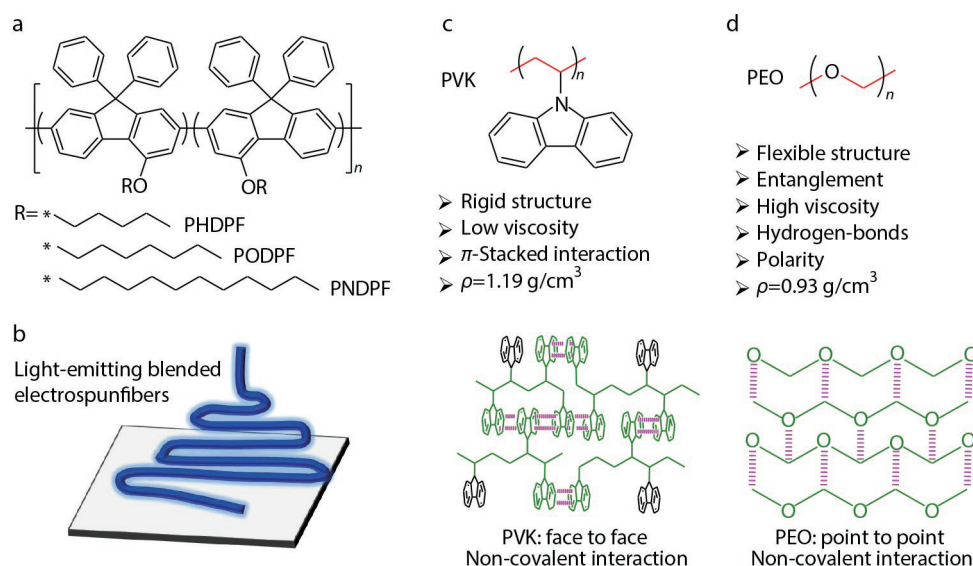
ther confirming the serious phase separation. And that also proves the lower interchain packing density due to the rigid backbone structure with a large free volume (Scheme 1c). Therefore, it is urgent to select a flexible matrix with a low free volume and high viscosity to improve the detection sensitivity of explosives. Compared with PVK chain, polyethylene oxide (PEO) has an excellent flexible backbone structure, hydrogen-bonded-assisted network and excellent interchain entanglement. So it is beneficial not only to improve the dispersion of LCPs but also to optimize the surface morphology of hybrid ES fibers (Scheme 1d).^[47,48] Therefore, in this work, we selected PEO as a matrix to prepare a series of polydiarylflorenes hybrid ES fibers, and then tune chain conformation and optimize the morphology of ES fibers to improve their sensing sensitivity (Scheme 1). As a result, different from polydiarylflorenes/PVK ES fibers with the rough surface and inefficient dispersion, polydiarylflorenes/PEO ES fibers show smooth surface morphology with a uniform deep-blue emission, which are useful to obtain a high emission efficiency of 60%. Finally, due to the small size, smooth surface and high emission efficiency, polydiarylflorenes/PEO ES fibers have a better sensing sensitivity to explosives than those of PVK ES fibers. This also confirms the effectiveness of our assumption.

EXPERIMENTAL

Experimental details are outlined in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

According to previous works,^[47,49] strong π - π stacking of pendant carbazoles (Cz) in PVK backbone structure are existed in the solid state, which was probed by the obvious and feature emission at 420–400 nm. Additionally, rigid aromatic structure of PVK also caused a serious phase separation between PVK and polydiarylflorenes. Therefore, with the rapid solvent evaporation, a number of pores and aggregates appeared on



Scheme 1 (a) Chemical structures of polydiarylflorenes used in this work. (b) Schematic diagram of light-emitting ES hybrid fibers from electrospinning setup. Unique physic-chemical properties of PVK (c) and PEO (d) as a matrix in electrospinning (ES) processing. Dash lines represent the non-covalent interactions, such as π - π interaction for PVK, hydrogen-bonding interaction for PEO.

the surface of PODPF/PVK ES fibers (Figs. 1a–1c). What is more, as fluorescent microscopic (FLM) images shown in Fig. 1(c), although PODPF/PVK ES fibers show a deep-blue emission, there are many nano-aggregate found in the ES fibers. These aggregate may be attributed to the formation of PODPF domain, which is the original driving force to induce the formation of planar (β) conformation in these ES fibers, similar to our previous work.^[50] On the other side, this inefficient dispersion also reveals the severe phase separation in the ES processing under rapid solvent evaporation. In contrary, purified PEO ES fibers have a smooth and continuous surface without any pores, which also indicates its excellent ES processing capacity (Fig. 1d). Similar to PEO system, the same smooth surface is also observed on the PODPF/PEO ES fibers (Fig. 1e). More interestingly, as shown in Fig. 1(f), the PODPF/PEO ES fibers display relatively uniform deep-blue emission, indicating that PODPF is evenly distributed in the fibers with almost no phase separation in the ES processing. Hydrogen-bonded-assisted network makes PEO show an excellent interchain entanglement, so that polydiarylfuorenes/ PEO precursor mixed solution with a certain viscosity can be obtained. And it is beneficial to suppress phase separation between them. In this regard, it is easy to conclude that this kind of flexible PEO with a dynamic network is conducive to preparing uniform and efficient LCPs ES hybrid fibers.

In order to further confirm this assumption, we also obtained a series of polydiarylfuorenes/PEO ES fibers, including PHDPP/PEO, PODPF/PEO and PNDPP/PEO. All the hybrid ES fibers were prepared from 1,2-dichloroethane (DCE) and chloroform (CHCl_3) solution. As displayed in Fig. 2 and Figs.

S1–S9 (in ESI), significantly different from the rough morphology of polydiarylfuorenes/PVK ones, all the polydiarylfuorenes/PEO hybrid ES fibers are a cylindrical-type nanowires with a uniform and smooth surface morphology. Interestingly, PHDPP/PEO and PNDPP/PEO ES hybrid fibers have a slightly small width with the diameter of $\sim 1 \mu\text{m}$. In addition, PODPF/PEO fibers prepared from DCE and CHCl_3 are similar in the size and surface morphology, with the diameter of $\sim 3 \mu\text{m}$, as shown in Fig. 2(d). More interestingly, these microfibers have uniform deep-blue emission. It shows that there is a weak phase separation between PEO and polydiarylfuorenes. In general, the emission efficiency and stability of optoelectronic materials can be effectively improved by suppressing the formation of aggregate. Cylindrical-type nanowires with a small size exhibited a high surface area to possibly react with the “acceptor” explosives molecules, which is useful to improve the detection sensitivity of explosives.

In general, the external traction force in ES processing can induce the molecular orientation along the fibers direction.^[43] Meanwhile, the rapid solvent evaporation also caused strong interchain aggregation and phase separation. These two factors have influence on the photophysical property of hybrid ES fibers. In order to investigate how to influence them, we also explored the emission spectra of various hybrid ES fibers. As displayed in Fig. 3(a), PL spectra of all ES fibers consisted of three emission peaks of about 440, 462 and 493 nm, respectively, assigned to the 0-0, 0-1, and 0-2 vibration transition of single polyfluorene chain.^[49] It revealed the feature non-planar conformation in amorphous fibers, which is similar to the previous PHDPP/PEO and PNDPP/PEO ones (Fig. 3a).

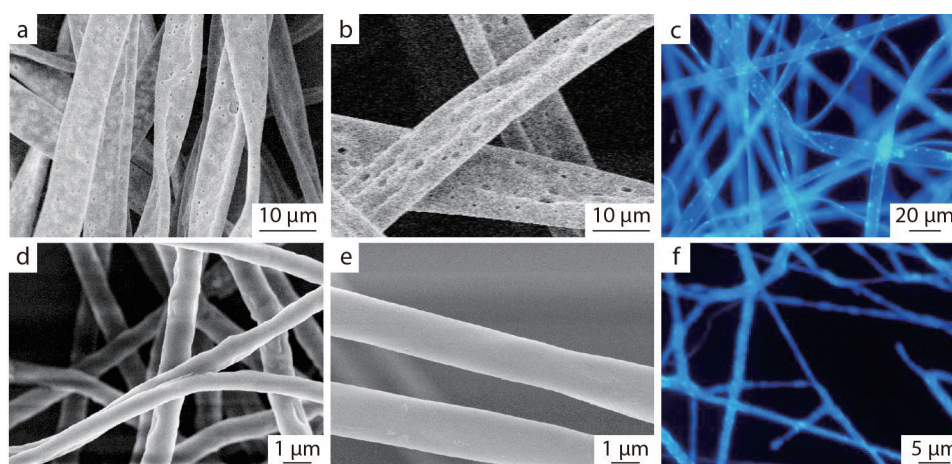


Fig. 1 FESEM images of PVK (a) and PODPF/PVK (b), PEO (d) and PODPF/PEO (e) electrospun fibers prepared from DCE solutions, together with the FLM images of PODPF/PVK (c) and PODPF/PEO (f).

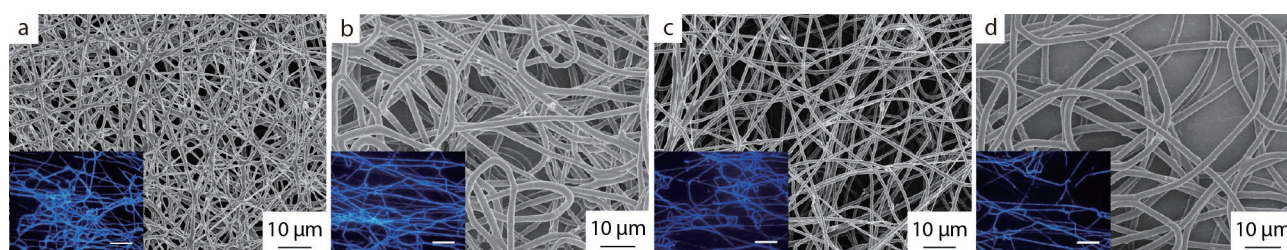


Fig. 2 FESEM images of PHDPP/PEO (a), PODPF/PEO (b) and PNDPP/PEO (c) electrospun fibers prepared from DCE solution, together with PODPF/PEO fibers (d) from CHCl_3 solution, respectively. Insets show their corresponding FLM images. Scale bar in FLM is about $120 \mu\text{m}$.

Interestingly, these hybrid ES fibers also show a robust deep-blue emission. As shown in Fig. 3(b), PL quantum yield (Φ_{PLQY}) of corresponding PHDPF/PEO, PODPF/PEO and PNDPF/PEO are estimated about 50%, 60% and 51%, respectively, and PODPF/PEO ES fibers prepared from CHCl_3 solution have a similar PLQY with a value of 53%. In this regard, PODPF/PEO ES fibers obtained from DCE solution show a slightly high PLQY, about ~20% than those of other three type fibers. Interestingly, there is a low fraction of planar (β) conformation formation in the PODPF/PEO ES fibers obtained from DCE solution. According to the excitation-wavelength dependent

PL spectra, well-resolved emission peaks at 457, 484 and 515 nm can be observed in the PL spectra excited at from 430 nm to 450 nm (Fig. 3c),^[51] owing to the 0-0, 0-1, and 0-2 vibration transition of β -conformation. This is an effective evidence to confirm the formation of β -conformation in these microfibrils. The maximum emission peak at 436 nm reveals a low fraction of β -conformation, which cannot trap all exciton and energy from non-planar conformation. As we expected, PL spectra of the PODPF/PEO obtained from CHCl_3 solution, PHDPF/PEO and PNDPF/PEO ES fibers obtained from DCE solution at 400–444 nm display no significantly difference be-

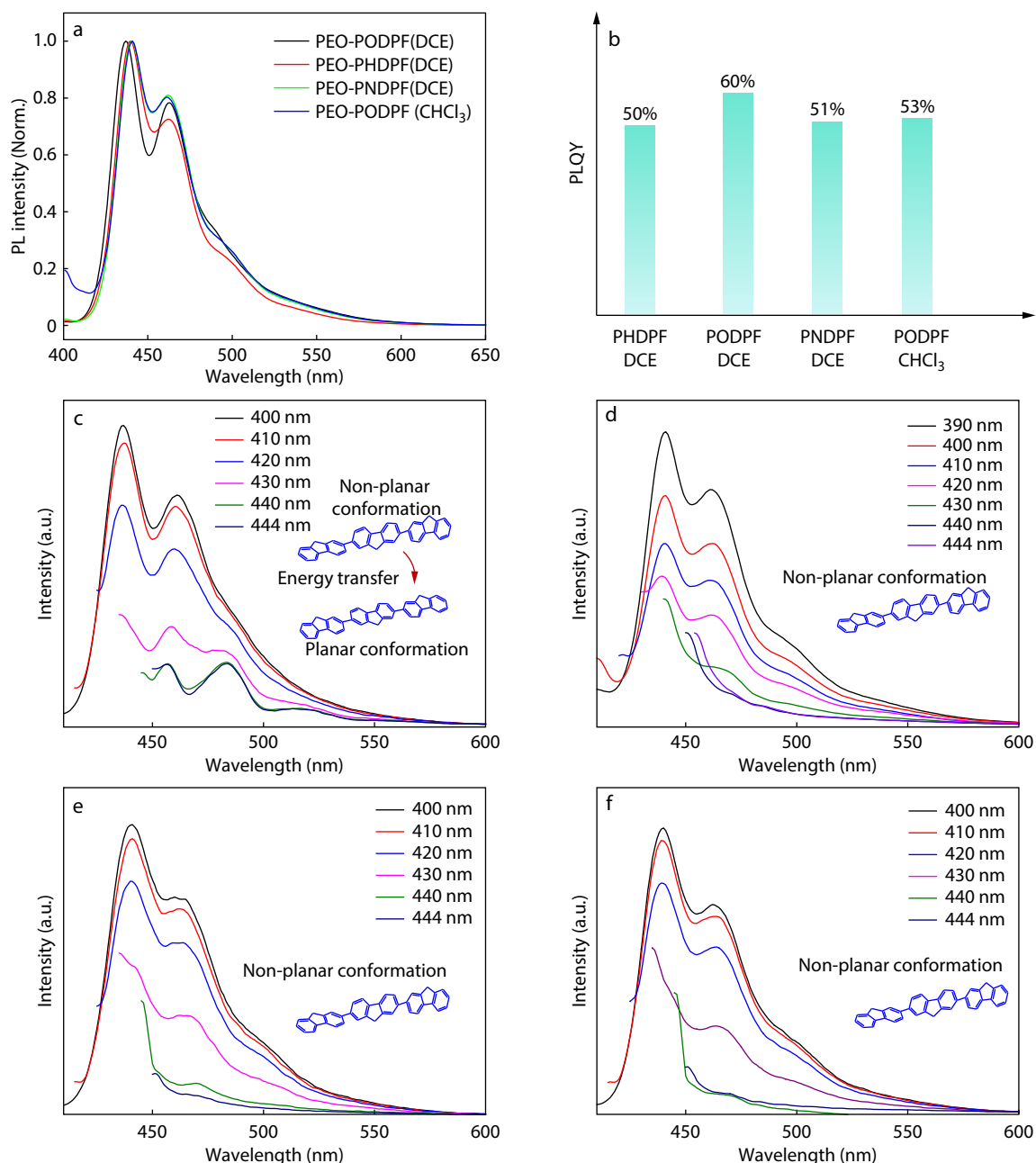


Fig. 3 (a) Emission spectra of PHDPF/PEO, PODPF/PEO and PNDPF/PEO electrospun fibers prepared from DCE solution, together with PODPF/PEO fibres from CHCl_3 solutions. Excitation wavelength is about 390 nm; (b) Corresponding photofluorescent quantum yield (PLQY) of various ES hybrid fibers; PL spectra of β -conformation-contained PODPF/PEO (DCE) electrospun fibers (c), amorphous PODPF/PEO (d), PHDPF/PEO (e) and PNDPF/PEO (f) electrospun fibers obtained from CHCl_3 at different wavelengths shown in the legend.

cause there is no β -conformation formation (Figs. 3d–3f).^[51–53] The previous experimental data results also indicated the octyl side chain enable PODPF to show a best chain complanation capacity, consistent with the previous works.^[41,54,55] In our previous work, it is also easily observed that the β -conformation with a relatively high fraction is obtained in the PODPF/PVK ES fibers. A number of PODPF aggregates appeared in the ES fibers, which reasonably explained this unique property (Fig. 1c).^[41] Interchain aggregation of PODPF provided an excellent molecular landscape to stabilize chain complanation. On the contrary, there is no obvious aggregate formation in the PODPF/PEO fibers. Therefore, the β -conformation in PODPF/PEO fibers may be induced by the external traction force in the ES processing. And this single chain with a planar conformation is useful to deep-blue emission with a high efficiency. Thus, it reasonably accounts for the relatively highest emission efficiency of PODPF/PEO fibers than those of the other three fibers. Meanwhile, efficient dispersion without obvious interchain aggregation will also enhance the emission efficiency, which is more conducive to expand their optoelectronic applications.

As we discussed above, smooth cylindrical-type PEO hybrid ES fibers with a small diameter display a high surface area.^[40,43,45] And the efficient dispersion of polyfluorene chain in PEO matrix can bring high emission efficiency, which is good for the exciton trapped by the acceptor explosive molecules. Subsequently, we set PODPF as an emissive centre to further investigate the exciton behavior of these polyfluorene/PEO and PVK hybrid ES fibers upon the explosive molecules. As displayed in Fig. 4(a), PODPF/PEO fibers have excellent feature emission behavior of single polyfluorene chain. Herein, the value of quenching efficiency is obtained via basing on ratio method, such as the ratio of emission intensity at start and stimulated states. When this kind of PODPF/PEO fibrous film was exposed to saturated DNT vapour, the emission intensity was severely quenched. Fig. 4(a) shows that the quenching intensity of PODPF/PEO ES fibers is about 45% after 5 min and 96% after 60 min. And it indicated that the excitons were mostly quenched by DNT molecules (Figs. S10–S12 in ESI). According to previous work, PODPF/PVK ES fibrous film have a relatively low quenching efficiency of

about 15% after 5 min and 58% after 60 min in saturated DNT vapours, as shown Fig. S10 (in ESI).^[41] Such a low detection sensitivity may be attributed to the rough surface morphology and large size of PODPF/PVK ES fibers.^[41] Besides, a number of nano-aggregates in PODPF/PVK ES fibers also inhibited the exciton of PODPF trapped by the DNT molecules. Exciton in the polyfluorene chain can be easily trapped by the DNT molecules, associated with the proper and match energy level to cause the exciton migration from polyfluorene chain to DNT molecules, which may reasonably explain this emission quenching. In this regard, the surface area of ES fiber is the key factor to the quenching efficiency. Therefore, as we expected, fluorescence quenching efficiency of PHDPF/PEO, PODPF/PEO and PNDPF/PEO ES fibers are about 85%, 96% and 95% (Figs. S11–S13 and Table S1 in ESI), respectively. Poor solubility of PHDPF with a short side chain may result in its relatively low sensitivity. And the small diameter of PNDPF/PEO ES fibers is also beneficial to obtain this high detection sensitivity. Short length of side-chain in PHDPF may cause low solubility to result into a serious aggregation upon solvent evaporation in electrospinning processing, which is no good for quenching efficiency. Excellent solubility of PNDPF is beneficial for optimizing the dispersion of chain in ES fiber and reducing the diameter of ES fiber. More importantly, under strong stretching forces, octyl-side chain at 4-position of fluorenes was the optimal chain length to induce the formation of β -conformation, in which the orientation of polymer chains along the long axis of the fiber and the planar backbone of conjugated polymer are beneficial to the π - π electronic interaction along the long-axis. Compared to PHDPF/PEO ones, PODPF/PEO ES fibers obtained from DCE solution with a larger diameter, also present a relatively higher quenching efficiency but slightly lower than those of PNDPF/PEO ES fibers. More interestingly, under the same diameter and surface morphology, PODPF/PEO ES fibers obtained from DCE solution show a slightly higher quenching efficiency than those of PODPF/PEO ES fibers obtained from CHCl_3 solution, which may be attributed to the synergistic effect of β -conformation and high deep-blue emission efficiency. The exciton energy migration along planar conformational chain can bring efficient sensing by quenchers. Finally,

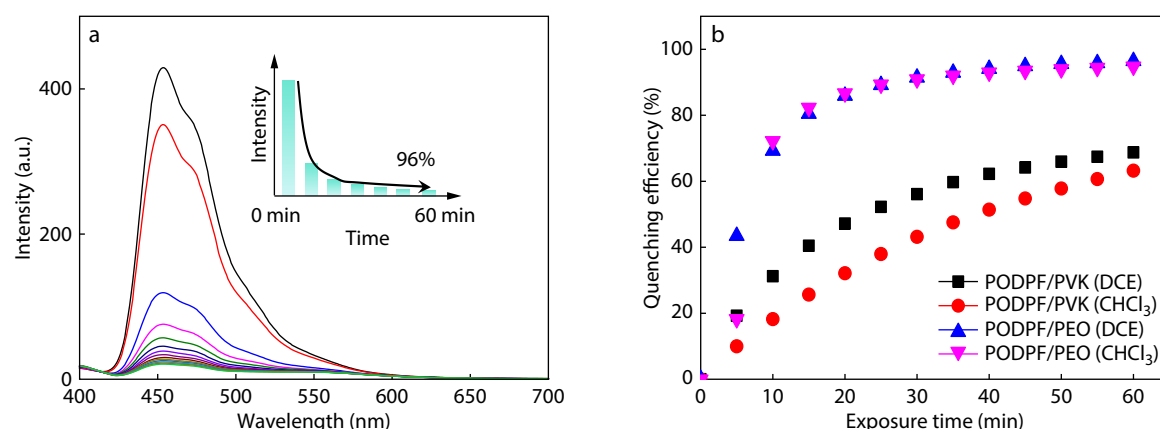


Fig. 4 Polydiarylfuorenes electrospun hybrid microfibers for detection of DNT explosives. (a) Time-dependent fluorescence quenching process of the β -conformational PODPF/PEO (DCE) fibrous film; (b) Time-dependent fluorescence quenching efficiency of PODPF/PVK, PODPF/PEO hybrid microfibers obtained from DCE and CHCl_3 solutions.

as presented in Fig. 4(b), both PODPF/PEO ES fibers prepared from DCE and CHCl_3 solution have a higher quenching efficiency. They are about 1.5-fold greater than those of PVK hybrid fibers. Therefore, it is easily and effectively concluded that the detection sensitivity of explosives can improve via controlling the hierarchical structure of LCPs.

CONCLUSIONS

In summary, a series of polydiaryluorenes/PEO ES hybrid microfibers with a smooth morphology are obtained via selecting flexible PEO as matrix. In contrast to rigid PVK matrix, these PEO hybrid ES fibers present a small diameter of $\sim 3 \mu\text{m}$ and smooth surface morphology. More interestingly, uniform and efficient deep-blue emission are also observed in all PEO ES fibers, which have an emission efficiency of $>50\%$. What's more, significantly different to the β -conformation caused by the interchain aggregation in PODPF/PVK ones, the PODPF chain can be also planarized in the PEO ES fibers assisted by external traction force in ES processing. Due to the small diameter and smooth morphology, PEO type hybrid ES fibrous films present a higher quenching efficiency than those of PVK ones. In this regard, it is an effective strategy to optimize hierarchical structure of hybrid polymeric system via selecting a proper matrix in ES processing.

Conflict of Interests

Wei Huang is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-2927-1>.

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REFERENCES

- Bai, L.; Han, Y.; Lin, J.; Xie, L.; Huang, W. Intrinsically stretchable conjugated polymers for flexible optoelectronic devices. *Sci. Bull.* **2021**, *66*, 2162–2164.
- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Light-emitting diodes based on conjugated polymers. *Nature* **1990**, *347*, 539–541.
- Ling, H.; Liu, S.; Zheng, Z.; Yan, F. Organic flexible electronics. *Small Meth.* **2018**, *2*, 1800070.
- Oh, J. Y.; Rondeau-Gagné, S.; Chiu, Y.-C.; Chortos, A.; Lissel, F.; Wang, G. J. N.; Schroeder, B. C.; Kurosawa, T.; Lopez, J.; Katsumata, T.; Xu, J.; Zhu, C.; Gu, X.; Bae, W. G.; Kim, Y.; Jin, L.; Chung, J. W.; Tok, J. B. H.; Bao, Z. Intrinsically stretchable and healable semiconducting polymer for organic transistors. *Nature* **2016**, *539*, 411–415.
- Swager, T. Polymer light-emitting devices-light from insulated organic wires. *Nat. Mater.* **2002**, *1*, 151–152.
- White, M. S.; Kaltenbrunner, M.; Glowacki, E. D.; Gutnichenko, K.; Kettlgruber, G.; Graz, I.; Aazou, S.; Ulbricht, C.; Egbe, D. A. M.; Miron, M. C.; Major, Z.; Scharber, M. C.; Sekitani, T.; Someya, T.; Bauer, S.; Sariciftci, N. S. Ultrathin, highly flexible and stretchable PLEDs. *Nat. Photon.* **2013**, *7*, 811.
- Zhang, Z.; Guo, K.; Li, Y.; Li, X.; Guan, G.; Li, H.; Luo, Y.; Zhao, F.; Zhang, Q.; Wei, B.; Pei, Q.; Peng, H. A colour-tunable, weavable fibre-shaped polymer light-emitting electrochemical cell. *Nat. Photon.* **2015**, *9*, 233.
- Yokota, T.; Zalar, P.; Kaltenbrunner, M.; Jinno, H.; Matsuhisa, N.; Kitano, H.; Tachibana, Y.; Yukita, W.; Koizumi, M.; Someya, T. Ultraflexible organic photonic skin. *Sci. Adv.* **2016**, *2*, e1501856.
- Liang, A.-H.; Zhang, K.; Zhang, J.; Huang, F.; Zhu, X. H.; Cao, Y. Supramolecular phosphorescent polymer iridium complexes for high-efficiency organic light-emitting diodes. *Chem. Mater.* **2013**, *25*, 1013–1019.
- Bai, L.; Han, Y.; Sun, C.; An, X.; Wei, C.; Liu, W.; Xu, M.; Sun, L.; Sun, N.; Yu, M.; Zhang, H.; Wei, Q.; Xu, C.; Yang, Y.; Qin, T.; Xie, L.; Lin, J.; Huang, W. Unveiling the effects of interchain hydrogen bonds on solution gelation and mechanical properties of diaryluorene-based semiconductor polymers. *Research* **2020**, *2020*, 3405826.
- Zhou, K.; Dai, K.; Liu, C.; Shen, C. Flexible conductive polymer composites for smart wearable strain sensors. *SmartMat* **2020**, *1*, e1010.
- Huang, W.; Meng, H.; Yu, W. L.; Gao, J.; Heeger, A. J. A new blue light-emitting polymer containing substituted thiophene and an arylene-1,3,4-oxadiazole moiety. *Adv. Mater.* **1998**, *10*, 593–596.
- Yu, W. L.; Meng, H.; Pei, J.; Huang, W. Tuning redox behavior and emissive wavelength of conjugated polymers by p-n diblock structures. *J. Am. Chem. Soc.* **1998**, *120*, 11808–11809.
- Heeger, A. J. Semiconducting and metallic polymers: the fourth generation of polymeric materials (Nobel Lecture). *Angew. Chem. Int. Ed.* **2001**, *40*, 2591–2611.
- Yao, Y.; Chen, Y.; Wang, H.; Samori, P. Organic photodetectors based on supramolecular nanostructures. *SmartMat* **2020**, *1*, e1009.
- Xie, L. H.; Yin, C. R.; Lai, W. Y.; Fan, Q. L.; Huang, W. Polyfluorene-based semiconductors combined with various periodic table elements for organic electronics. *Prog. Polym. Sci.* **2012**, *37*, 1192–1264.
- Kim, B.-G.; Jeong, E. J.; Chung, J. W.; Seo, S.; Koo, B.; Kim, J. A molecular design principle of lyotropic liquid-crystalline conjugated polymers with directed alignment capability for plastic electronics. *Nat. Mater.* **2013**, *12*, 659–664.
- Facchetti, A. Made to order. *Nat. Mater.* **2013**, *12*, 598–600.
- Diao, Y.; Tee, B. C. K.; Giri, G.; Xu, J.; Kim, D. H.; Becerril, H. A.; Stoltenberg, R. M.; Lee, T. H.; Xue, G.; Mannsfeld, S. C. B.; Bao, Z. Solution coating of large-area organic semiconductor thin films with aligned single-crystalline domains. *Nat. Mater.* **2013**, *12*, 665–671.
- Treat, N. D.; Nekuda Malik, J. A.; Reid, O.; Yu, L.; Shuttle, C. G.; Rumbles, G.; Hawker, C. J.; Chabiny, M. L.; Smith, P.; Stingelin, N. Microstructure formation in molecular and polymer semiconductors assisted by nucleation agents. *Nat. Mater.* **2013**, *12*, 628–633.
- Venkateshvaran, D.; Nikolka, M.; Sadhanala, A.; Lemaire, V.; Zelazny, M.; Kepa, M.; Hurhangee, M.; Kronemeijer, A. J.; Pecunia, V.; Nasrallah, I.; Romanov, I.; Broch, K.; McCulloch, I.; Emin, D.;

- Olivier, Y.; Cornil, J.; Beljonne, D.; Sirringhaus, H. Approaching disorder-free transport in high-mobility conjugated polymers. *Nature* **2014**, *515*, 384–388.
- 22 Spano, F. C.; Silva, C. H- and J-aggregate behavior in polymeric semiconductors. *Annu. Rev. Phys. Chem.* **2014**, *65*, 477–500.
- 23 Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. About supramolecular assemblies of pi-conjugated systems. *Chem. Rev.* **2005**, *105*, 1491–1546.
- 24 Haedler, A. T.; Klaus, K.; Abey, I.; Bernd, W.; Milan, K.; Natalie, H.; Jürgen, K.; Hans-Werner, S.; Richard, H. Long-range energy transport in single supramolecular nanofibres at room temperature. *Nature* **2018**, *523*, 196–199.
- 25 Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P. V.; Stingelin, N.; Smith, P.; Toney, M. F.; Salleo, A. A general relationship between disorder, aggregation and charge transport in conjugated polymers. *Nat. Mater.* **2013**, *12*, 1038.
- 26 Dong, H.; Hu, W. Multilevel investigation of charge transport in conjugated polymers. *Acc. Chem. Res.* **2016**, *49*, 2435–2443.
- 27 Heeger, A. J. Semiconducting polymers: the Third Generation. *Chem. Soc. Rev.* **2010**, *39*, 2354–2371.
- 28 Wang, Y.; Yang, J.; Gong, Y.; Fang, M.; Li, Z.; Tang, B. Z. Host-guest materials with room temperature phosphorescence: tunable emission color and thermal printing patterns. *SmartMat* **2020**, *1*, e1006.
- 29 Zhang, X.; Hu, Q.; Lin, J.; Lei, Z.; Guo, X.; Xie, L.; Lai, W.; Huang, W. Efficient and stable deep blue polymer light-emitting devices based on β -phase poly(9,9-dioctylfluorene). *Appl. Phys. Lett.* **2013**, *103*, 153301.
- 30 Xu, M.; Yu, M.; Liu, B.; Lin, J.; Soleimaninejad, H.; Smith, T. A.; Ding, X.; Bai, L.; Han, Y.; Xie, L.; Liu, W.; Ghiggino, K. P.; Lin, Z.; Yu, T.; Xu, C.; Huang, W. Hierarchical uniform crystalline nanowires of wide bandgap conjugated polymer for light-emitting optoelectronic devices. *Cell Rep. Phys. Sci.* **2020**, *1*, 100029.
- 31 Yu, M. N.; Lin, J. Y.; Li, Y. X.; Soleimaninejad, H.; Ou, C. J.; Bai, L. B.; Liu, B.; Liu, W.; Wei, Q.; Bo, Y. F.; Smith, T. A.; Dunstan, D. E.; Ghiggino, K. P.; Xie, L. H.; Xu, C. X.; Bradley, D. D. C.; Huang, W. Emission enhanced and stabilized by stereoisomeric strategy in hierarchical uniform supramolecular framework. *Chem* **2019**, *5*, 2470–2483.
- 32 Ou, C.; Cheetham, N. J.; Weng, J.; Yu, M.; Lin, J.; Wang, X.; Sun, C.; Cabanillas-Gonzalez, J.; Xie, L.; Bai, L.; Han, Y.; Bradley, D. D. C.; Huang, W. Hierarchical uniform supramolecular conjugated spherulites with suppression of defect emission. *iScience* **2019**, *16*, 399–411.
- 33 Hao, X.-T.; McKimmie, L. J.; Smith, T. A. Spatial fluorescence inhomogeneities in light-emitting conjugated polymer films. *J. Phys. Chem. Lett.* **2011**, *2*, 1520–1525.
- 34 Shaw, P. E.; Ruseckas, A.; Peet, J.; Bazan, G. C.; Samuel, I. D. W. Exciton-exciton annihilation in mixed-phase polyfluorene films. *Adv. Funct. Mater.* **2010**, *20*, 155–161.
- 35 Yang, F.; Sun, L.; Duan, Q.; Dong, H.; Jing, Z.; Yang, Y.; Li, R.; Zhang, X.; Hu, W.; Chua, L. Vertical-organic-nanocrystal-arrays for crossbar memristors with tuning switching dynamics toward neuromorphic computing. *SmartMat* **2021**, *2*, 99–108.
- 36 Ding, X. H.; Chang, Y. Z.; Ou, C. J.; Lin, J. Y.; Xie, L. H.; Huang, W. Halogen bonding in the co-crystallization of potentially ditopic diiodotetrafluorobenzene: a powerful tool for constructing multicomponent supramolecular assemblies. *Natl. Sci. Rev.* **2020**, *7*, 1906–1932.
- 37 He, B.; Li, J.; Bo, Z.; Huang, Y. Highly polarized blue luminescence from the oriented poly(9,9-dioctylfluorene)/polyethylene blending films. *Macromolecules* **2005**, *38*, 6762–6766.
- 38 Podzorov, V. Conjugated polymers: Long and winding polymeric roads. *Nat. Mater.* **2013**, *12*, 947–948.
- 39 Camposo, A.; Persano, L.; Pisignano, D. Light-emitting electrospun nanofibers for nanophotonics and optoelectronics. *Macromol. Mater. Eng.* **2013**, *298*, 487–503.
- 40 Xue, W.; Xu, M.; Yu, M. N.; Sun, H. M.; Lin, J. Y.; Jiang, R. C.; Xie, L. H.; Shi, N. E.; Huang, W. Electrospun supramolecular hybrid microfibers from conjugated polymers: color transformation and conductivity evolution. *Chinese J. Polym. Sci.* **2021**, *39*, 824–830.
- 41 Xue, W.; Lin, J. Y.; Liu, B.; Shi, N. E.; Yu, M. N.; Wu, W. D.; Zhu, W. S.; Xie, L. H.; Wang, L. H.; Huang, W. Exploring side-chain length effect on β -phase of polyfluorene derivatives in electrospinning and their optical behavior. *Polymer* **2018**, *153*, 338–343.
- 42 Vohra, V.; Giovannella, U.; Tubino, R.; Murata, H.; Botta, C. Electroluminescence from conjugated polymer electrospun nanofibers in solution processable organic light-emitting diodes. *ACS Nano* **2011**, *5*, 5572–5578.
- 43 Agarwal, S.; Greiner, A.; Wendorff, J. H. Functional materials by electrospinning of polymers. *Prog. Polym. Sci.* **2013**, *38*, 963–991.
- 44 Xie, Z.; Xie, K.; Hu, T.; Ma, J.; Zhang, J.; Ma, R.; Cheng, X.; Li, J.; Hu, Z. Multi-wavelength coherent random laser in bio-microfibers. *Opt. Express* **2020**, *28*, 5179–5188.
- 45 Xie, L. H.; Yang, S. H.; Lin, J. Y.; Yi, M. D.; Huang, W. Fluorene-based macromolecular nanostructures and nanomaterials for organic (opto)electronics. *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences* **2012**, *371*, 20120337.
- 46 Scherf, U.; List, E. J. W. Semiconducting polyfluorenes—towards reliable structure-property relationships. *Adv. Mater.* **2002**, *14*, 477–487.
- 47 Xie, L. H.; Ling, Q. D.; Hou, X. Y.; Huang, W. An effective Friedel-Crafts postfunctionalization of poly(N-vinylcarbazole) to tune carrier transportation of supramolecular organic semiconductors based on pi-stacked polymers for nonvolatile flash memory cell. *J. Am. Chem. Soc.* **2008**, *130*, 2120–2121.
- 48 An, X.; Liu, W.; Bai, L. B.; Sun, L. L.; Xu, M.; Xie, L. H.; Song, L.; Xu, C. X.; Yang, Y. G.; Liu, B.; Lin, J. Y.; Huang, W. Long-range ordered hierarchical structure assisted by the side-oligoether network in light-emitting conjugated polymer for an efficient deep-blue organic laser. *Chem. Mater.* **2021**, *33*, 5326–5336.
- 49 Lin, J.; Liu, B.; Yu, M.; Wang, X.; Lin, Z.; Zhang, X.; Sun, C.; Cabanillas-Gonzalez, J.; Xie, L.; Liu, F.; Ou, C.; Bai, L.; Han, Y.; Xu, M.; Zhu, W.; Smith, T. A.; Stavrinou, P. N.; Bradley, D. D. C.; Huang, W. Ultrastable supramolecular self-encapsulated wide-bandgap conjugated polymers for large-area and flexible electroluminescent devices. *Adv. Mater.* **2019**, *31*, 1804811.
- 50 Lin, Z. Q.; Shi, N. E.; Li, Y. B.; Qiu, D.; Zhang, L.; Lin, J. Y.; Zhao, J. F.; Wang, C.; Xie, L. H.; Huang, W. Preparation and characterization of polyfluorene-based supramolecular π -conjugated polymer gels. *J. Phys. Chem. C* **2011**, *115*, 4418–4424.
- 51 Bai, L.; Liu, B.; Han, Y.; Yu, M.; Wang, J.; Zhang, X.; Ou, C.; Lin, J.; Zhu, W.; Xie, L.; Yin, C.; Zhao, J.; Wang, J.; Bradley, D. D. C.; Huang, W. Steric-hindrance-functionalized polydiarylflorenes: conformational behavior, stabilized blue electroluminescence, and efficient amplified spontaneous emission. *ACS Appl. Mater. Interfaces* **2017**, *9*, 37856–37863.
- 52 Liu, B.; Lin, J. Y.; Liu, F.; Yu, M. N.; Zhang, X.; Xia, R.; Yang, T.; Fang, Y.; Xie, L.; Huang, W. A highly crystalline and wide-bandgap polydiarylflorene with β -phase conformation toward stable electroluminescence and dual amplified spontaneous emission. *ACS Appl. Mater. Interfaces* **2016**, *8*, 21648–21655.
- 53 Lin, J. Y.; Zhu, W. S.; Liu, F.; Xie, L. H.; Zhang, L.; Xia, R.; Xing, G. C.; Huang, W. A rational molecular design of β -phase polydiarylflorenes: synthesis, morphology, and organic lasers. *Macromolecules* **2014**, *47*, 1001–1007.
- 54 Liu, B.; Lin, J. Y.; Yu, M. N.; Li, B.; Xie, L.; Ou, C.; Liu, F.; Li, T.; Lu, D.; Huang, W. Hereditary character of alkyl-chain length effect on β -phase conformation from polydialkylfluorenes to bulky polydiarylflorenes. *J. Phys. Chem. C* **2017**, *121*, 19087–19096.
- 55 Bright, D. W.; Dias, F. B.; Galbrecht, F.; Scherf, U.; Monkman, A. P. The influence of alkyl-chain length on beta-phase formation in polyfluorenes. *Adv. Funct. Mater.* **2009**, *19*, 67–73.