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Solvatochromism, Reversible Chromism and Self-Assembly Effects of Heteroatom-Assisted Aggregation-Induced Enhanced Emission (AIEE) Compounds

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Abstract: Two compounds, 9,10-bis[2-(quinolyl)vinyl]anthracene (BQVA) and 9,10-bis[2-(naphthalen-2-yl)vinyl]anthracene (BNVA), have been synthesised and investigated. Both of them have aggregation-induced enhanced emission (AIEE) properties. Heteroatom-assisted BQVA shows solvatochromism, reversible chromism properties and self-assembly effects. When increasing the solvent polarities, the green solution of BQVA turns to orange with a redshift of the fluorescence emission wavelengths from $\lambda = 527$ to 565 nm. Notably, BQVA exhibits reversible chromism properties, including mechano- and thermochromism. The as-prepared BQVA powders show green fluorescence ($\lambda_{em} = 525$ nm) and the colour can turn into orange ($\lambda_{em} = 573$ nm) after grinding. Interestingly, the orange colour can return at high tempera-

Introduction

Organic chromic luminescent materials, including thermochromic, pizeochromic and other "smart" materials, have attracted increasing attention by virtue of their extensive applications in anti-counterfeiting of brands, temperature/pressure sensor films and so forth.^[1–3] Although changing the chemical structures is the most effective way to control the chromic processes, both low reaction efficiency and irreversibility in the solid state mean that this way is not suitable for exploitation and applications.^[4] Notably, controlling the physical state of aggregations is easier to achieve colour changes in the materials by using external forces.^[5–7] However, most chromic luminescent materials suffer from aggregation-caused quenching (ACQ) effects in the solid state, which ultimately limit the development of chromic materials.^[8]

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ture. Based on these reversible chromism properties, a simple and convenient erasable board has been designed. Different from BQVA, non-heteroatom-assisted BNVA has no clear chromic processes. The results obtained from XRD, differential scanning calorimetry, single-crystal analysis and theoretical calculations indicate that the chromic processes depend on the heteroatoms in BQVA. Additionally, BQVA also exhibits excellent self-assembly effects in different solvents. Homogeneous nanospheres are formed in mixtures of tetrahydrofuran and water, which are then doped into silica nanoparticles and treated with 3-aminopropyltriethoxysilane to give amino-functionalised nanoparticles (BQVA–AFNPs). The BQVA–AFNPs could be used to stain protein markers in polyacrylamide gel electrophoresis.

The fall-known aggregation-induced emission (AIE) or aggregation-induced enhanced emission (AIEE) phenomena reported by Tang and co-workers in 2001 effectively overcome the interference of ACQ, and have become popular topics in many materials fields.^[9] To date, abundant AIE/AIEE materials have been reported,^[10] such as hexaphenylsilole (HPS),^[11] tetraphenylethene (TPE),^[12] distyrylanthracene (DSA)^[13, 14] and their derivatives. The AIE/AIEE materials possess amazing properties, for instance, high quantum yields, controlled self-assembly effects and photostabilities,^[15-17] which result in potential applications in organic light-emitting diodes (OLEDs) materials,^[18] label-free bioprobes,^[19,20] bioimaging^[21] and so on. Interestingly, many AIE/AIEE materials can respond to external stimuli, including pressure, temperature and solvent vapours. It is worth mentioning that many reported TPE and HPS derivatives possess multi-chromism properties.^[22-26] In addition, DSA derivatives that possess piezo- and thermochromism have been reported,^[27] although the solvatochromism of DSA derivatives is still restricted. General mechanisms of chromism are considered to be associated with changes in the molecular packing modes and crystallinities in external environments.^[28,29] However, the design and synthesis of AIE/AIEE molecules, the molecular packing modes of which are easily and reversibly changed by external stimuli, is still a challenge. Hence, it is essential to introduce new synthetic methods for AIE/AIEE chromic luminescent materials.

Abundant AIE/AIEE materials possess self-assembly effects.^[18,30] It is important to expand the biological application

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ranges of self-assembly effects, although there a few biocompatible AIE/AIEE materials have been reported; these expand the biological applications.^[31-33] The idea of combining AIE/AIEE materials and polymers to obtain organic fluorescent nanoparticles (OFNs) with enhanced water solubilities and biocompatibilities would greatly broaden the applications of AIE/ AIEE materials in biofields.^[34] However, these OFNs rely on special chemical reactions between appropriate AIE/AIEE compounds and polymers.^[35] Thus, reports on AIE-based OFNs are rare. Another way of preparing OFNs is to use silica because silica is known to be biocompatible and easy to modify.[36,37] AIE/AIEE materials are able to self-assemble into regular aggregates in mixed solvents. Therefore, coating these aggregates with silica layers provides a new approach to prepare more biocompatible OFNs and greatly broadens their bioapplications.

Herein, inspired by acceptor– π –A (A- π -A) structures, we have synthesised and investigated the heteroatom-assisted AIEE compound 9,10-bis[2-(quinolyl)vinyl]anthracene (BQVA). It shows excellent solvatochromism, reversible chromism and self-assembly effects at the same time. With increasing water fractions, the fluorescence (FL) intensity of suspensions is enhanced 10-fold and the emission colours change from green to orange. Owing to the A- π -A structure of BQVA, it possesses remarkable solvatochromism characteristics, along with enhancement of the solvent polarities, and the emission bands redshift from $\lambda = 527$ to 565 nm. The as-prepared powders show a green emission under UV light and after mechanical grinding the solids show an orange emission. This colour change can be recovered by thermal stimulation. We also synthesised non-heteroatom-assisted 9,10-bis[2-(naphthalen-2-yl)vinyl]anthracene (BNVA) for comparison. The results show that BNVA only has AIEE properties and no chromism properties. The XRD, differential scanning calorimetry (DSC), crystal structure and theoretical calculations results confirm that heteroatoms in BQVA play an important role in multi-chromism. Firstly, the heteroatoms in BQVA lead to the A- π -A structure, which induces solvatochromism. Secondly, the nitrogen atoms make it possible for intermolecular C-H-N bonds to exist and stabilise the molecular sheets in the BQVA packing structures. These molecular sheets will slip under external stimulus, such as pressure or temperature, which results in reversible multi-chromism. The results confirm the significance of heteroatoms in the multi-chromism AIEE materials, they also provide new ideas for the design and exploration of more materials with these properties. In addition, we also used the self-assembled nanoparticles (NPs) of BQVA in mixtures of THF/water to prepare silicacoated OFNs, and amination modification to give amino-functionalised nanoparticles (BQVA-AFNPs). Finally, we used them to stain protein markers in the gel after 1D polyacrylamide gel electrophoresis (PAGE). The preparation of BQVA-AFNPs provides a new method to prepare more biocompatible AIEE-OFNs and broadens the bioapplications of self-assembly effects.

Results and Discussion

We synthesised BQVA and BNVA through the Witting–Horner reaction. The general synthetic route is shown in Scheme S1 in the Supporting Information. The compounds were characterised by ¹H NMR spectroscopy, MALDI-TOF MS and elemental analysis. The optimised molecular structures were calculated by DFT calculations (B3LYP/6-31G). Figure 1 shows the chemical and optimised molecular structures. The results suggest that both optimised molecular structures of BQVA and BNVA are highly twisted, which makes it possible for them to possess AIEE properties.

BQVA and BNVA are soluble in common organic solvents, such as acetone, THF and dichloromethane (DCM). To further confirm their AIEE characterisation, we chose acetone and THF as the good solvents and water as the poor solvent. Figure S1 in the Supporting Information shows the absorption spectra of BQVA in mixtures of acetone and water; the concentrations of the suspension are 100 μ M. The absorption maximum (λ_{abs}) of a solution of BQVA in acetone is $\lambda \approx$ 423 nm. When the water fraction, $f_{\rm w}$, is 30%, $\lambda_{\rm abs}$ remains at the same wavelength, whereas the intensity is stronger than that in solution. When f_w reaches 50%, the absorption intensity at $\lambda =$ 423 nm is reduced greatly. In the suspension with more water ($f_w = 70\%$), the intensity at $\lambda = 423$ nm disappears, while a weak band appears at $\lambda \approx 460$ nm. When f_w is as high as 90%, a remarkable absorption band at $\lambda =$ 460 nm represents the formation of BQVA aggregates in suspensions. The absorption spectra of BQVA are in accordance with the FL spectra, as shown in Figure 2A and B.

With increasing f_{w} the FL intensities are enhanced 10-fold and the emission wavelengths are redshifted. In mixtures of acetone/water with a low water content (\leq 30%), the FL signals are weak at $\lambda =$ 565 nm. The FL intensity of the suspension $(f_w = 50\%)$ increases dramatically; the emission wavelength is $\lambda = 510$ nm with a green colour under a UV lamp. With $f_{\rm w}$ increasing to 70%, the suspension shows a yellow emission at λ \approx 556 nm. In the suspensions with the highest water contents $(f_w = 90\%)$, the emission wavelength continuously redshifts to $\lambda =$ 562 nm with a strong orange emission. The results indicate that BQVA has AIEE and colour-tuning characteristics. Similar AIEE behaviour can be observed under the same conditions as those used for BQVA. Figure S2 in the Supporting Information shows the absorption spectra of BNVA in mixtures of acetone/ water with different water fractions. Due to its poor solubility in acetone, the absorption intensity is weaker than that of BQVA. In acetone, BNVA shows an absorbance band at $\lambda =$ 408 nm, which is blueshifted by 15 nm relative to BQVA. This blueshift implies that naphthyl has a weaker electronwithdrawing ability than quinolyl. When water is added, suspensions of BNVA show no absorbance band. The disappearance of the absorption also proves the generation of BNVA aggregates in mixtures of acetone/water. The FL intensity of the suspension ($f_w = 50\%$) is 1.5 times stronger than that of the solution ($f_w = 0$ %). Different from BQVA, the emission wavelength is redshifted by only 5 nm (from $\lambda = 539$ to 544 nm), and the emission colour remains yellow-green with various f_{w}

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Figure 1. A) Chemical, and B) optimised molecular structures of BQVA. C) Chemical, and D) optimised molecular structures of BNVA.



Figure 2. A) FL spectra, and B) corresponding FL intensity of BQVA in mixtures of acetone/water with different f_w excited at $\lambda = 365$ nm. C) FL spectra, and D) corresponding FL intensity of BNVA under the same conditions. The insets show the corresponding emission colours under UV illumination. Suspension concentrations: 100 μ M.

The absorption results for BQVA and BNVA in mixtures of THF/ water with different fractions (0, 30, 50, 70 and 90%) are also determined (Figures S3 and S4 in the Supporting Information). The results indicate that the solubility of BNVA in THF is better state electron distribution. In contrast, the FL spectra (Figure 4) show a remarkable redshift ($\lambda = 527$ to 565 nm): with solvents varying from hexane to acetone, the emission colours also vary from green to yellow to orange. We also determined the pho-

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than that in acetone. With high water fractions, the absorption bands of BQVA and BNVA redshift remarkably, which represents the formation of aggregates. The FL spectra (Figure 3) further confirm the AIEE properties.

Quinolyl possesses a stronger electron-withdrawing ability than naphthyl. Quinolyl groups make it possible for BQVA to have A-π-A structures. In general, molecules with donor-acceptor (D-A) structures exhibit solvatochromism when they are excited in solvents. We examined the absorption and FL spectra of BQVA in six solvents with different polarities. The results are shown in Table S1 in the Supporting Information. Along with the growing solvent polarities, λ_{abs} of BQVA redshifts from $\lambda=$ 420 to 425 nm. The slight changes in λ_{abs} of BQVA suggest that the polarities of the solvents have little effect on the ground-



Figure 3. A) FL spectra, and B) corresponding FL intensity of BQVA in mixtures of THF/water with different f_w excited at $\lambda = 365$ nm. C) FL spectra, and D) corresponding FL intensity of BNVA under the same conditions. The insets show the corresponding emission colours under UV illumination. Suspension concentrations: 100 μ M.



Figure 4. Absorption (dashed lines) and FL (excited at $\lambda = 365$ nm, solid lines) spectra of BQVA in different solvents. The inset shows the corresponding emission properties under illumination with a UV lamp.

tophysics of BNVA in same solvents and observe opposite phenomena. Figure S5 in the Supporting Information shows that the absorption spectra, FL spectra and emission colours of BNVA in various solvents are slightly altered. Thus, the polarities of the solvents have a slight effect on both the groundand excited-state electron distributions of BNVA. This is possible due to the absence of D-A structures in BNVA.

To further determine the solvent effects on BQVA, we investigated the linear correlation between the Stokes shift (Δv) and solvent polarity parameter (Δf) calculated by using the Lippert–Mataga equation. Figure S6 in the Supporting Information shows that the slope of the fitting line gives a value of 2885.5, which suggests satisfactory solvatochromism. Additionally, we used the Reichardt equation to investigate the relationships between emission wavelengths and empirical parameters; this gave a slope of 98.1 (Figure S6 in the Supporting Information). According to the good results from the two methods, we confirmed that BQVA had remarkable solvatochromic properties.

Organic chromic luminescent materials have attracted much attention because of their extensive applications. In addition of solvatochromism, we investigated the mechano- and thermochromism properties of BQVA and BNVA. The results are shown in Figure 5.

Figure 5 A shows photographs of initial and ground powders of BQVA taken under RL and UV. The initial powders of BQVA are yellow with green emission under UV illumination. After being mechanically ground, the yellow powders changed into orange powders, with emission colours varying from green to

orange under UV illumination. Figure 5B exhibits the corresponding FL spectra; the emission wavelengths of as-prepared and ground powders are $\lambda = 525$ and 573 nm, respectively. These results demonstrate that BQVA possesses mechanochromism properties. In addition, BQVA has thermochromatic abilities. As shown in Figure 5A, the colours of ground powders return to the initial colours after being heated at 130°C. To further study the chromic effects of BOVA, we determined the recyclability between two emission powders (Figure 5C). BQVA demonstrates excellent recyclability after five grinding and heating cycles. In contrast to BQVA, BNVA shows inconspicuous mechano- and thermochromatic properties. The initial and ground powders are orange under RL and yellow under UV. The FL spectra (Figure 5E) show that after grinding the emission wavelength redshifts by only 10 nm (from $\lambda = 546$ to 556 nm). Although BNVA displays good repeatability between grinding and heating (Figure 5F), considering its unchanged colours, we conclude that BNVA molecules are not mechano- and thermochromism materials. Based on the good chromism properties of BQVA, we applied it in a simple and convenient erasable board (Figure 6).

On the other hand, BQVA and BNVA possess high thermal decomposition temperatures (T_{dr} , corresponding to 5% weight loss) of 366.02 and 398.13 °C (Figures S8 and S9 in the Supporting Information). The good T_{d} results give them potential to be luminogens for OLEDs. For BQVA, in particular, its multichromism and high T_{d} make it possible for BQVA to be used as an effective material in many fields.

To explain the chromatic mechanisms of BQVA, we used powder X-ray diffraction (PXRD) to determine the patterns of





Figure 5. A) Photographs of initial and ground powders of BQVA taken in room light (RL) and under UV light (UV). B) FL spectra of initial and ground powders of BQVA, excited at $\lambda = 365$ nm. C) Reversible switching of emission wavelengths of BQVA after repeated grinding and heating cycle. D) Photographs of initial and ground powders of BNVA taken under RL and UV. E) FL spectra of initial and ground powders of BNVA, excited at $\lambda = 365$ nm. F) Reversible switching of emission wavelengths of BNVA after repeated grinding and heating cycles. The heating temperature was 130 °C.

H=Heat G=Grind W=Write





amorphous state, along with redshifts of the emission. The pat-

Figure 6. Photographs of writing and erasing on an erasable board with

Figure 7. XRD patterns of initial powders, ground powders and heated powders for: A) BQVA, and B) BNVA.

cule is highly twisted; the dihedral angle between the anthracene and quinoline planes is nearly 90°. The twisted structure is stabilised by 16 intermolecular forces of the type C–H··· π (d=2.846 Å, 2.834 Å), C–H···N (d=2.665 Å) and π - π (d= 3.315 Å). All forces are shown in Figure S12 in the Supporting

tern changes for BQVA were also studied by DSC. The results in Figure S10 in the Supporting Information indicate that there is an endothermic peak at around 240 °C in the DSC curve of the initial powder. A new exothermic peak appears in the DSC curve of the ground powder. This new peak indicates the metastable amorphous state of the ground powder.^[39]

According to previous reports, molecules are often more twisted in the crystalline state than in the amorphous state.^[28] We used crystal and electronic structures to further study chromic processes. The solvent diffusion method was used to prepare the crystals. A clubbed and greenemitting crystal suitable for X-ray analysis was obtained from saturated solutions in THF placed in petroleum ether (Figure S11 in the Supporting Information). This crystal belongs to the monoclinic system. The crystal structures, intermolecular forces and packing structures are shown in Figure 8. The results reveal that the green-emitting BQVA mole-

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BQVA coated on filter paper.

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Figure 8. A) Single-crystal structure and intermolecular forces of BQVA. B) Packing mode of BQVA in the single crystal.

Information. The forces prevent rotation and strong π - π interactions in the BQVA molecule, reduce non-radiative decay and result in the strong green emission.

Figure 8B shows the packing mode of BQVA in the single crystal. Molecular sheets are formed in the packing structures. The sheets are stabilised by intermolecular C–H···N bonds (Figure S13 in the Supporting Information). These molecular sheets are able to slip under external stimuli, such as pressure or temperature.^[40] When stimulated by pressure, the packing structures are destroyed and the transformation of the molecules from the crystalline state to an amorphous state results in the redshift of the emission. After heating, both the packing structures and emission colour are restored. These results are in agreement with the PXRD results. Because no C–H···N bonds exist in BNVA molecules, we infer that there is no easy slippage of the molecular sheets and BNVA cannot possess multiple chromism properties.

We also used DFT calculations at the B3LYP/6-31G level to calculate the distributions of the HOMO and LUMO energies of BQVA (crystal structure), BQVA (optimised structure) and BNVA (optimised structure). Figure S14 in the Supporting Information reveals that the crystal structure of BQVA has a higher degree of twisting and lower degree of conjugation than those of the optimised structure. This implies that the crystal structure has stronger torsional stress than that of the optimised structure. Figure 9 shows the corresponding electron cloud distributions. The calculated orbital energy gaps of crystal and optimised structures are 0.119 and 0.107 eV. The higher energy of the crystal structure confirms its instability, which contributes to its multiple chromism characteristics. In addition, the molecular



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Figure 9. Electron cloud distribution of frontier molecular orbitals of BQVA (crystal structure), BQVA (optimised structure) and BNVA (optimised structure).

conformation of the optimised structure is more planar than that of the crystal structure; better co-planarity of BQVA after grinding will also lead to the redshifted emission.^[28] The energy gaps of BQVA and BNVA in the optimised structures are same (0.107 eV), so it can be inferred that BQVA in its optimised structures shows a yellow emission.

Because AIE or AIEE molecules usually show interesting selfassembly characteristics,^[30] we used the method of evaporation-induced self-organisation (EISO) to prepare self-assembled structures. The results were characterised by SEM and FL microscopy, and all suspensions were 100 µм. Figure 10 shows that the self-assembled structures are induced by solvents. The morphologies of BQVA in mixtures of THF/water with $f_w = 90\%$ are nanospheres with diameters of approximately 200 nm. When the solvent was a mixture of THF/petroleum ether ($f_p =$ 90%), BQVA molecules self-assembled into structured microrods. Figure 10D shows that the emission colour of the microrods is green. When BQVA molecules are dissolved in THF, they organise into flower-like structures (Figure 10C). The results provide a new way to control the self-assembly of AIEE molecules. On the other hand, the structured morphologies also prove the regular conformations of BQVA. We acquired crystals of BQVA from microcrystalline structures in mixtures of THF/petroleum ether, whereas the preparation of BNVA crystals failed.

The fabrication of NPs for bioapplications is very important. Considering that nanospheres formed in mixtures of THF/ water, we doped these nanospheres into silica NPs to prepare fluorescent nanoparticles (FNPs). Figure 11 A shows the related schematic illustration. To enhance the hydrophilicity, we used 3-aminopropyltriethoxysilane (APTES) to give BQVA-AFNPs. To demonstrate that BQVA-AFNPs can supply accurate detection of proteins, we applied BQVA-AFNPs to stain protein markers in the gel after 1D PAGE, and used the conventional protein detection method of CBB-R250 staining as a reference.^[41] The protein markers include thyroglobulin, ferritin, catalase, lactate dehydrogenase and albumin. From the results in Figure 11 C, we can see that both methods, traditional CBB-R250 staining and new BQVA-AFNPs FL imaging, can detect the five protein makers with different molecular masses. We conclude that the new method of BQVA-AFNPs FL imaging has potential applications in protein detection in gels after PAGE.



Figure 10. SEM micrographs of the self-assembled structures of BQVA generated by mixtures of: A) THF/water ($f_w = 90\%$); inset scale bar: 100 nm, B) THF/petroleum ether ($f_p = 90\%$); inset scale bar: 100 nm; and C) THF; D) FL microscopy images of BQVA generated in mixtures of THF/petroleum ether ($f_p = 90\%$).



Figure 11. A) Schematic illustration of the synthesis of BQVA-AFNPs and their application for protein visualisation after PAGE. CTAB = cetyltrimethylammonium bromide, TEOS = tetraethyl orthosilicate. B) TEM imaging of BQVA-AFNPs dispersed in water (scale bar: 200 nm). C) Detection of standard proteins after 1D PAGE with BQVA-AFNPs (left) and CBB-R250 (right).

Conclusion

We synthesised and investigated the AIEE compound BQVA, which possessed solvatochromism, reversible chromism and self-assembly effects at the same time. To confirm the critical role of heteroatoms in the chromism process, we used BNVA, in which non-heteroatoms exist, for comparison with BQVA. Results from XRD, single-crystal analysis and theoretical calculations revealed that nitrogen atoms in BQVA played an important role. BQVA had typical A- π -A structures, which contributed to the solvatochromism characteristics. In addition, intermolecular C–H···N bonds stabilised molecular sheets in the BQVA packing structures. When stimulated by the external en-

vironment, these molecular sheets slipped easily and induced reversible chromism. Additionally, we used the self-assembly effects of BQVA to prepare BQVA–AFNPs, and applied them in the staining of protein markers in a gel after PAGE. The preparation of BQVA–AFNPs broadens the bioapplications of self-assembly effects. Overall, we not only prepared new chromic AIEE "smart" materials, but also shed some light on introducing heteroatoms into AIE/AIEE molecules to prepare multi-chromic AIE/AIEE luminogens.

Experimental Section

Synthesis of 9,10-bis(dichloromethyl)anthracene

A two-necked, round-bottomed flask (500 mL) was oven-dried and cooled under a nitrogen atmosphere. Anthracene (9 g, 0.05 mol) and paraformaldehyde (7.6 g) were dissolved in 1,4-dioxane (72 mL) and hydrochloric acid (12 mL). The mixture was stirred for 2 h at 110 °C under the HCl atmosphere. After removal of the HCl gas, the reaction was stirred for 5 h at 110 °C. After being cooled to room temperature, the resulting precipitate was filtered and washed with 1,4-dioxane to give a yellow product (38%). ¹H NMR (400 MHz, CDCl₃): δ = 8.40–8.38 (m, 4H), 7.67–7.65 (m, 4H), 5.61 ppm (s, 4H).

Synthesis of tetraethylanthracene-9,10-diylbis(methylene)diphosphonate

9,10-Bis(dichloromethyl)anthracene (7.5 g, 25 mmol) was dissolved in triethylphosphate (50 mL) and added to an oven-dried, onenecked, round-bottomed flask (250 mL). The mixture was stirred for 24 h at 150 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, then the resulting precipitate was filtered and washed with petroleum ether to give the light-yellow product (70%). ¹H NMR (400 MHz, CDCl₃): δ = 8.39–8.37 (m, 4H), 7.58–7.56 (m, 4H), 4.29–4.21 (d, 4H), 3.93–3.77 (m, 8H), 1.08–1.05 ppm (m, 12H).

Synthesis of BQVA

Tetraethylanthracene-9,10-diylbis(methylene)diphosphonate (1 a, 2.08 mmol) and tBuOK (1 g, 9 mmol) were dissolved in dry THF (40 mL) under a nitrogen atmosphere. 2-Quinolinecarbaldehyde (1 g, 6.34 mmol) in dry THF (40 mL) was added dropwise to this mixture at room temperature and stirred for 12 h. The resulting precipitate was filtered and washed with methanol to give the bright-yellow product (30%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.68$ – 8.64 (d, J=16.3 Hz, 2 H), 8.50-8.47 (m, 4 H), 8.24-8.22 (d, J=8.5 Hz, 2H), 8.18-8.16 (d, J=8.4 Hz, 2H), 7.86-7.84 (d, J=8.1 Hz, 2H), 7.81-7.79 (d, J=8.5 Hz, 2H), 7.78-7.74 (m, 2H), 7.57-7.50 (m, 6H), 7.31–7.27 ppm (d, J = 16.4 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): $\delta =$ 155.5, 148.4, 137.7, 136.6, 132.5, 131.3, 129.8, 129.53, 129.47, 127.61, 127.57, 126.5, 126.4, 125.6, 119.8 ppm; MALDI-TOF MS: m/ z: 485.5 [M+H]⁺; elemental analysis calcd (%) for C₃₆H₂₄N₂: C 89.26, H 4.96, N 5.78; found: C 90.11, H 4.71, N 5.18.

Synthesis of BNVA

Tetraethylanthracene-9,10-diylbis(methylene)diphosphonate (1 g, 2.08 mmol) and tBuOK (1 g, 9 mmol) were dissolved in dry THF (40 mL) under a nitrogen atmosphere. 2-Naphthaldehyde(1 g, 6.40 mmol) in dry THF (40 mL) was added dropwise to this mixture at room temperature and stirred for 12 h. The resulting precipitate



was filtered and washed with methanol to give the orange-yellow product (39%). ¹H NMR (400 MHz, CDCl₃): δ =8.48–8.46 (m, 4H), 8.07–8.01 (d, *J*=24.2 Hz, 2H), 7.99–7.94 (m, 6H), 7.91–7.88 (d, *J*=12.5 Hz, 4H), 7.53–7.50 (m, 8H), 7.15–7.11 ppm (d, *J*=8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ =137.6, 136.3, 128.6, 128.3, 128.2, 127.8, 127.7, 127.6, 126.6, 126.54, 126.48, 125.50, 125.4, 123.3, 122.6, 119.7 ppm; MALDI-TOF MS: *m/z*: 483.2 [*M*+H]⁺; elemental analysis calcd (%) for C₃₈H₂₆: C 94.60, H 5.39; found: C 95.01, H 4.99.

Preparation of BQVA-AFNPs

CTAB (0.10 g, 0.27 mmol) was dissolved in ultrapure water (200 mL). An aqueous solution of NaOH (2.00 m, 0.36 mL) and BQVA (0.10 g, 0.11 mmol) in THF (5 mL) was added to the solution of CTAB 80 °C. Then TEOS (1.00 mL) and APTES (150 μ L) were added dropwise to the mixture under vigorous stirring. The mixture was allowed to react for 5 h. The white precipitate was filtered, washed with deionised water and methanol several times and dried to give BQVA–AFNPs.

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- [1] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* 2002, 420, 759–760.
- [2] M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev.* **2009**, *109*, 5755–5798.
- [3] S. Hirata, T. Watanabe, Adv. Mater. 2006, 18, 2725-2729.
- [4] D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martínez, S. R. White, *Nature* 2009, 459, 68–72.
- [5] H. Ito, T. Saito, N. Oshima, N. Kitamura, S. Ishizaka, Y. Hinatsu, M. Wakeshima, M. Kato, K. Tsuge, M. Sawamura, J. Am. Chem. Soc. 2008, 130, 10044–10045.
- [6] J. Luo, L. Y. Li, Y. Song, J. Pei, Chem. Eur. J. 2011, 17, 10515-10519.
- [7] M. Osawa, I. Kawata, S. Igawa, M. Hoshino, T. Fukunaga, D. Hashizume, *Chem. Eur. J.* 2010, 16, 12114–12126.
- [8] S. W. Thomas, G. D. Joly, T. M. Swager, Chem. Rev. 2007, 107, 1339– 1386.
- [9] Y. Q. Dong, J. W. Lam, A. J. Qin, Z. Li, J. Z. Liu, J. Z. Sun, Y. P. Dong, B. Z. Tang, Chem. Phys. Lett. 2007, 446, 124–127.
- [10] J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu, B. Z. Tang, *Chem. Commun.* 2001, 1740–1741.
- [11] R. R. Hu, N. L. C. Leung, B. Z. Tang, Chem. Soc. Rev. 2014, 43, 4494–4562.
- [12] H. Tong, Y. N. Hong, Y. Q. Dong, M. Häußler, J. W. Y. Lam, Z. Li, Z. Guo, Z. F. Guo, B. Z. Tang, *Chem. Commun.* **2006**, 3705–3707.
- [13] Z. J. Zhao, D. D. Liu, F. Mahtab, L. Y. Xin, Z. F. Shen, Y. Yu, C. Y. K. Chan, P. Lu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, B. Yang, Y. G. Ma, B. Z. Tang, *Chem. Eur. J.* **2011**, *17*, 5998–6008.

- [14] H. G. Lu, B. Xu, Y. J. Dong, F. P. Chen, Y. W. Li, Z. F. Li, J. T. He, H. Li, W. J. Tian, *Langmuir* **2010**, *26*, 6838–6844.
- [15] J. T. He, B. Xu, F. P. Chen, H. J. Xia, K. P. Li, L. Ye, W. J. Tian, J. Phys. Chem. C 2009, 113, 9892–9899.
- [16] X. G. Gu, J. J. Yao, G. X. Zhang, D. Q. Zhang, Small 2012, 8, 3406-3411.
- [17] Z. J. Zhao, J. W. Y. Lam, C. Y. K. Chan, S. M. Chen, J. Z. Liu, P. Lu, M. Rodriguez, J. L. Maldonado, G. Ramos-Ortiz, H. H. Y. Sung, L. D. Williams, H. M. Su, K. S. Wong, Y. G. Ma, H. S. Kwok, H. Y. Qiu, B. Z. Tang, *Adv. Mater.* **2011**, *23*, 5430–5435.
- [18] G. F. Zhang, H. F. Wang, M. P. Aldred, T. Chen, Z. Q. Chen, X. G. Meng, M. Q. Zhu, Chem. Mater. 2014, 26, 4433–4446.
- [19] J. Chen, Y. Wang, W. Y. Li, H. P. Zhou, Y. X. Li, C. Yu, Anal. Chem. 2014, 86, 9866–9872.
- [20] Y. N. Hong, M. Hauβler, J. W. Y. Lam, Z. Li, K. K. Sin, Y. D. Dong, H. Tong, J. Z. Liu, A. J. Qin, R. Renneberg, B. Z. Tang, *Chem. Eur. J.* **2008**, *14*, 6428–6437.
- [21] E. G. Zhao, Y. N. Hong, S. J. Chen, C. W. T. Leung, C. Y. K. Chan, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, Adv. Healthcare Mater. 2014, 3, 88–96.
- [22] Z. F. Chang, L. M. Jing, C. Wei, Y. P. Dong, Y. C. Ye, Y. S. Zhao, J. L. Wang, *Chem. Eur. J.* 2015, 21, 8504–8510.
- [23] Y. P. Zhang, D. D. Li, Y. Li, J. H. Yu, Chem. Sci. 2014, 5, 2710-2716.
- [24] J. Q. Tong, Y. J. Wang, J. Mei, J. Wang, A. J. Qin, J. Z. Sun, B. Z. Tang, Chem. Eur. J. 2014, 20, 4661–4670.
- [25] Q. K. Qi, J. Y. Qian, S. Q. Ma, B. Xu, S. X. A. Zhang, W. J. Tian, Chem. Eur. J. 2015, 21, 1149–1155.
- [26] Q. K. Qi, J. B. Zhang, B. Xu, B. Li, S. X. A. Zhang, W. J. Tian, J. Phys. Chem. C 2013, 117, 24997–25003.
- [27] X. Q. Zhang, Z. G. Chi, B. J. Xu, L. Jiang, X. Zhou, Y. Zhang, S. W. Liu, J. R. Xu, Chem. Commun. 2012, 48, 10895 10897.
- [28] Y. J. Dong, B. Xu, J. B. Zhang, X. Tan, L. J. Wang, J. L. Chen, H. G. Lv, S. P. Wen, B. Li, L. Ye, B. Zou, W. J. Tian, *Angew. Chem. Int. Ed.* **2012**, *51*, 4607–4612; *Angew. Chem.* **2012**, *124*, 4685–4690.
- [29] R. H. Li, S. Z. Xiao, Y. Li, Q. F. Lin, R. H. Zhang, J. Zhao, C. Y. Yang, K. Zou, D. S. Li, T. Yi, Chem. Sci. 2014, 5, 3922–3928.
- [30] C. X. Niu, L. Zhao, T. Fang, X. B. Deng, H. Ma, J. X. Zhang, N. Na, J. S. Han, J. Ouyang, *Langmuir* 2014, *30*, 2351–2359.
- [31] F. F. Wang, J. Y. Wen, L. Y. Huang, J. J. Huang, J. Ouyang, Chem. Commun. 2012, 48, 7395 – 7397.
- [32] H. Tong, Y. N. Hong, Y. Q. Dong, M. Haussler, Z. Li, J. W. Y. Lam, Y. P. Dong, H. H. Y. Sun, I. D. Williams, B. Z. Tang, J. Phys. Chem. C 2007, 111, 11817–11823.
- [33] M. C. Zhao, M. Wang, H. J. Liu, D. S. Liu, G. X. Zhang, D. Q. Zhang, D. B. Zhu, *Langmuir* **2009**, *25*, 676–678.
- [34] Z. K. Wang, S. J. Chen, J. W. Y. Lam, W. Qin, R. T. K. Kwok, N. Xie, Q. L. Hu, B. Z. Tang, J. Am. Chem. Soc. 2013, 135, 8238–8245.
- [35] X. Q. Zhang, M. Y. Liu, B. Yang, X. Y. Zhang, Y. Wei, Colloids Surf. B 2013, 112, 81–86.
- [36] Z. L. Wang, B. Xu, L. Zhang, J. B. Zhang, T. H. Ma, J. B. Zhang, X. Q. Fu, W. J. Tian, *Nanoscale* **2013**, *5*, 2065 – 2072.
- [37] X. Zhang, X. Zhang, S. Wang, M. Liu, Y. Zhang, L. Tao, Y. Wei, ACS Appl. Mater. Interfaces 2013, 5, 1943–1947.
- [38] Y. J. Dong, J. B. Zhang, X. Tan, L. J. Wang, J. L. Chen, B. Li, L. Ye, B. Xu, B. Zou, W. J. Tian, *J. Mater. Chem. C* 2013, *1*, 7554–7559.
- [39] Q. K. Qi, Y. F. Liu, X. F. Fang, Y. M. Zhang, P. Chen, Y. Wang, B. Yang, B. Xu, W. J. Tian, S. X. A. Zhang, *RSC Adv.* **2013**, *3*, 7996–8002.
- [40] S. J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M. G. Choi, D. Kim, S. Y. Park, J. Am. Chem. Soc. 2010, 132, 13675 13683.
- [41] P. P. Liu, N. Na, L. Y. Huang, D. C. He, C. G. Huang, J. Ouyang, Chem. Eur. J. 2012, 18, 1438–1443.

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