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ARTICLE

Construction of multi-layered white emitting organic nanoparticles by clicking polymers

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A series of blue, green and red emitting polymers that are appropriately functionalized with alkyne and azide functional groups have been prepared and clicked together to construct a bi-layered and tri-layered white emitting core-shell type nanoparticles. Here it was also demonstrated the use of these organic hetero-nanoparticles as colour converters to realize a white light-emitting diode platform acquiring a colour quality comparable to existing phosphor-based ones.

Introduction

White organic light emitting diodes (WOLEDs), either in pixelated arrays or over large areas have attracted great attention from both scientific community and industry owing to their superior properties potentially for the next-generation of curved-panel displays and surface lighting applications.¹⁻³ Due to their low-cost, high-efficiency, flexible and eco-friendly qualities, current research efforts have been devoted to the synthesis of novel material for WOLEDs to reduce global energy consumption.^{4,5} Since Kido *et al.* reported multilayer WOLED, several strategies are now being employed to generate light covering the visible range of the spectrum as much as possible.⁶⁻⁹ To obtain emission across the visible spectrum, a set of different fluorophores are utilized each with distinct emission colours. These typically involve two (blue and green/yellow) or three (blue, green and red) fluorophores.¹⁰⁻¹³

Recent decades have witnessed the introduction of a number of electro and photoactive conjugated polymers, such as polythiophene (PT), poly(p-phenylenevinylene) (PPV), and polyfluorene (PF). Polyfluorene and its derivatives stand out as a suitable material for polymer light emitting diode (PLED) due to their high quantum efficiencies, superior thermal stabilities and the availability of the hydrogen on the 9th position of fluorene for functionalization.¹⁰⁻¹⁷ As a blue emitter with high

quantum efficiency, polyfluorene serves as donor to other lower energy acceptor molecules mainly through non-radiative energy transfer.¹⁵⁻¹⁷ Non-radiative energy transfer or Förster resonance energy transfer (FRET) is an efficient and rapid process which is aided by the coupled dipole-dipole interaction between donor and acceptor molecules.¹⁸ Numerous studies also investigated energy transfer in hybrid systems involving donor polymer molecules and acceptor dye molecules for various applications.^{19,20} Since synthetic procedures such as copolymerization can have undesirable effect on emission characteristic of the original conjugated polymer, a novel approach to harness and tune the distinct emission of different fluorophores for OLEDs have long being sought.^{17, 21-23} Foulger *et al.* demonstrated emission colour tuning in hybrid bi-polymer nanoparticles for optoelectronic and imaging applications.²⁴

Taking advantage of the efficient energy transfer and emission colour tuning in bi-polymer nanostructures, we present a tunable white-emitting conjugated polymer nanoparticles (CPN).²⁵⁻²⁸ The emission properties can both be controlled by varying acceptor concentration and nanostructure design. Recent studies in our group showed an efficient energy transfer in polyfluorene with poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as an acceptor in the form of bi-polymer nanoparticles.²⁹ However, in this aforementioned work non-functionalized blue and green emitting polymers were utilized to assemble core-shell type nanostructures. Devoid of functional groups on the polymers and as a result of specific interactions between the layers resulted in the less efficient energy transfer and generation of low quality white light emission.

In this work, we prepared bi-layered and tri-layered white emitting core-shell type nanoparticles by clicking light emitting polymers through alkyne-azide 1,3-dipolar cycloaddition. Although white emission can be generated using bi-layered polymer nanoparticles, tri-layered polymer nanoparticles have

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better white light qualities due to its wider coverage of the spectrum. This approach allowed us to tune the emission colour and the quality of the white light by adjusting the nanoparticles (NPs) composition and the energy transfer as well as to obtain stable and shape persistent nanoparticles that remain intact in different solvents because of the cross-linking of functional groups through click chemistry.

Results and discussion

We have prepared a series of conjugated polymers emitting in the region of blue, green and red. The molecular structures of these polymers are shown in Figure 1. As can be seen from their structures, these polymers contain alkyne and azide functional groups that can undergo 1,3-dipolar cycloaddition to form triazole rings while cross-linking the polymers during core-shell type nanoparticle formation.

Blue emitting polymer, PFB-N3 was synthesized from the reaction of precursor polymer PFB-Br with nucleophilic substitution of sodium azide (ESI, Fig. S1). The synthesis and characterization of PFB-Br were reported in our previous publications.³⁰⁻³¹ The green emitting polymer, PFBT-P was synthesized upon functionalization of the precursor polymer PFBT-Br with excess propargyl alcohol in the presence of base and in DMF (ESI, Fig. S2). PFBT-Br was obtained through Suzuki coupling of fluorene monomer and benzothiadiazole as reported in previous studies.^{27,32,33} Finally, red emitting polymer PTH-N3 was synthesized by treating PTH-Ts with sodium azide in DMF. PTH-Ts was prepared by the Stille coupling of 2-(2,5-dibromothiophen-3-yl)ethyl-4-methylbenzenesulfonate and 5,5'-bis(tributylstannyl)-2,2'-bithiophene (ESI, Scheme S1). Synthesis and characterization details of PTH-N3 with NMR, FTIR and GPC were given in the supporting information section (ESI, Fig.S3-S5).

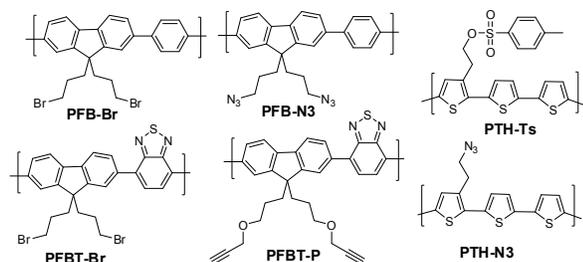


Fig. 1. Molecular structure of polymers used in this work.

Bi-polymer nanoparticles

Here four different designs were investigated in order to obtain white emitting bi-polymer nanoparticles as schematically shown in Figure 2. The first method involves physically mixing donor and acceptor nanoparticles. For this, first blue and green emitting nanoparticles were prepared using reprecipitation method. Briefly, blue or green emitting polymers were dissolved in THF and separately injected into rapidly stirring excess water. After stirring for a while to let the nanoparticle form, THF was removed under reduced pressure. The two

nanoparticles were then mixed and denoted NP mixed. For the second design, PFB-N3 (D) PFBT-P (A) polymers were dissolved in THF and ultrasonicated for 10 min. The solution of polymers was injected into a large excess of rapidly stirring water and the mixture was further sonicated for 40 min. and then THF was removed under reduced pressure to obtain stable bi-polymer nanoparticles. The resulting nanoparticle was denoted Soln NPs.

In the third method, sequentially formed bi-polymer nanoparticles were designed. Core nanoparticle (PFB-N3) was first prepared (contain azide functional groups and emit blue) and then green emitting polymer (PFBT-P) solution was added (alkyne containing) to form shell. The resulting bi-polymer nanoparticles, donor being core and surrounded with 45 mol% acceptor polymer was denoted DA45%. Also DA10% and DA62% were prepared similarly with the same donor concentration but varying the acceptor concentrations as 10 mol% and 62 mol% of acceptor polymer, respectively. Fourth method, which is quite the reverse of the third method; core nanoparticles (PFBT-P) was first prepared (alkyne containing and emits green) and then blue emitting polymer solution (PFB-N3) was added (azide containing) to form shell. The resulting bi-polymer nanoparticles was denoted AD 45%, acceptor being core and surrounded with donor.

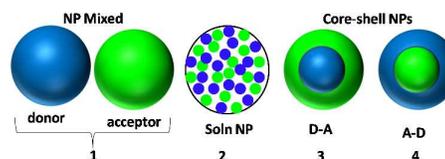


Fig. 2 Illustration of the four bi-polymer NP designs

In addition, catalytic amount of CuSO_4 and sodium ascorbate was added to facilitate click reaction in these designs. Another set of these designs were prepared without using Cu(I) catalyst in order to see whether 1,3-dipolar cycloaddition would still be taking place.

Size and morphologies of these nanoparticles were determined by SEM, TEM and DLS. Images and DLS histograms were provided in the supporting information (ESI, Table S1, Fig. S6). The average size of PFBN3, PFBT and PTN3 nanoparticles were determined by DLS measurement to be 64 nm, 63 nm and 80 nm respectively.

In order to prove that the 1,3-dipolar cycloaddition between azide and alkyne functional groups are taking place in the presence and absence of Cu(I) catalyst, we recorded FT-IR spectra of the nanoparticles. The FTIR spectra of some bi-polymer nanoparticles are compared with the spectra of PFBN3 nanoparticles (donor) and PFBT nanoparticles (acceptor) in Figure 3. The donor which are functionalized with azide groups show a strong stretching band of azide at 2098 cm^{-1} . When donor and acceptor nanoparticles were mixed physically (denoted as NP Mixed), a broad stretching band of azide was observed as well; this indicates that click reaction does not take place between the functional groups of donor and acceptor nanoparticles when they are mixed physically. Interestingly, in

the case of bipolymer nanoparticles prepared by click reaction which are catalyzed with Cu(I) (DA 10 and DA 45) or without catalyst (cDA 45), the azide stretching band at 2098 cm^{-1} disappeared indicating the formation of triazole ring from azides and alkynes. During the core-shell type nanoparticle formation, even in the absence of Cu(I) catalyst 1,3-dipolar cycloaddition is taking place. The reason could be explained by the proper alignment of the alkyne and azide groups because it is expected most of these groups to be located on the surface of core nanoparticles; this, in turn, allows them to be in close proximity to react faster.

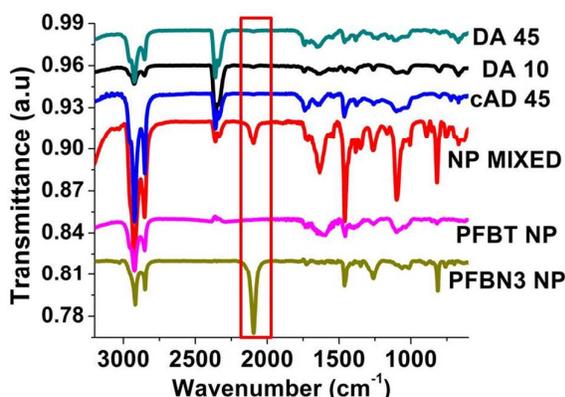


Fig. 3 FTIR (solid state, KBr pellet) spectra of bi-polymer Nanoparticles. The degree of click reaction was determined to be 97% for DA 45, 95% for cDA45 and 88% for DA10.

In a bid to synthesize white emitting bi-polymer nanoparticles, four nanostructure designs were investigated. PFBN3 and PFBT polymers were utilized as donor and acceptor pair, respectively, so as to study energy transfer dependent on nanoparticles morphology and design.³² Using FRET, we seek to tune the emission of the hybrid nanoparticles to white, which has potential applications in solid state lighting. First, photophysical properties of donor and acceptor polymer nanoparticles were investigated in order to find out whether they are suitable for FRET studies. The absorbance and fluorescence spectra of PFB-N3 (donor) in THF and PFB-N3 nanoparticles in water are given in Figure 4(a). The donor peak emission wavelength is $\sim 420\text{ nm}$ when they are dispersed in water to form nanoparticles, while the absorbance and emission bands of PFBT-P nanoparticles (acceptor) is 444 nm and 544 nm respectively (Figure 4b). In Figure 4d, the overlay of donor and acceptor spectra show a strong spectral overlap between donor emission and absorbance of acceptor for FRET in bi-polymer nanoparticles. In addition, PTH-N3 was utilized as a red emitting polymer to design tandem nanoparticles. The peak emission of PTH-N3 is $\sim 620\text{ nm}$ when dispersed in water to form nanoparticles (Figure 4c).

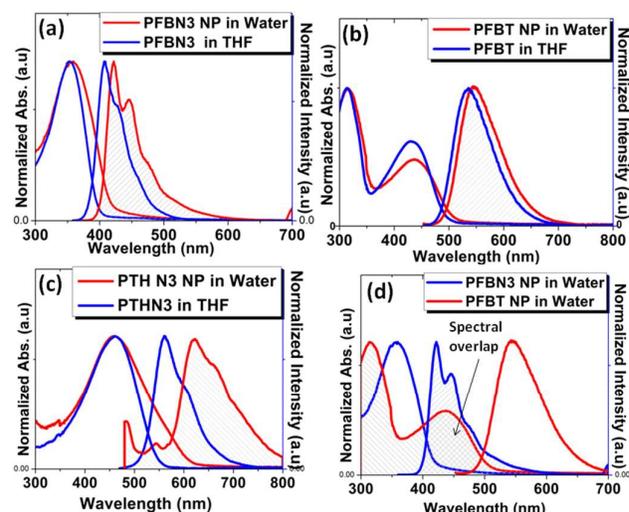


Fig. 4 Absorbance and emission spectra of conjugated polymers in THF and in water (a) PFBN3 in THF and PFB-N3 CPNs in water (b) PFBT-P in THF and PFBT CPNs in water (c) PTH-N3 in THF and PTH-N3 CPNs in water (d) Overlay of spectra show a strong spectral overlap between PFB-N3(donor) and PFBT-P (acceptor)

In the first bi-polymer nanoparticles design (Figure 5a), separately formed nanoparticles were mixed with the ratio of 55 mol% donor and 45 mol% acceptor. With respect to donor and acceptor nanoparticles alone, there was no significant change in the optical properties of the mixed nanoparticles. The emission spectrum shows two peaks at 420 nm and 544 nm corresponding to the exact emission of donor and acceptor nanoparticles alone respectively. However, the emission at 544 nm in mixed nanoparticles does suggest that there is energy transfer from donor to acceptor. When the emission intensity at 350 nm excitation is compared with the emission intensity at 435 nm excitation, a ratio of 0.81 was calculated. This ratio means that there is no strong FRET due to large distance between donor and acceptor in solution when the nanoparticles are physically mixed later.

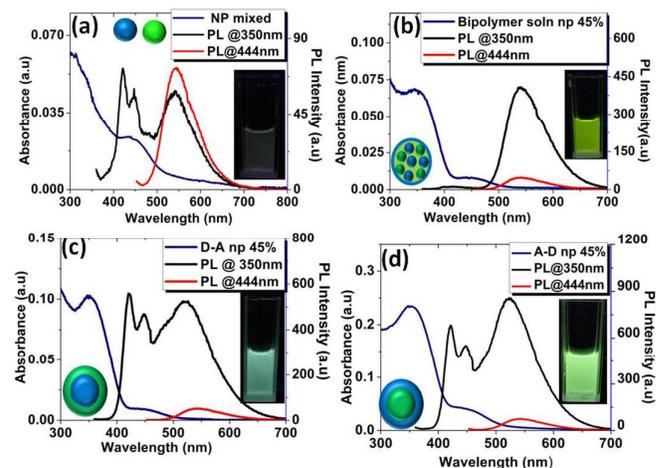


Fig. 5 Absorbance and emission spectra of bipolymer NP dispersion in water (a) NP Mixed (PFB-N3+PFBT-P NPs) (b) Soln NP (mixing the two polymers solutions prior to NP formation) (c) DA 45 NP (PFB-N3/PFBT-P) (d) AD 45 NP (PFBT-P/PFB-N3) (λ_{ex} =350 nm)

For the second bi-polymer nanoparticles design (Figure 5b), where solutions of donor and acceptor were mixed prior to nanoparticles formation, a 5 nm blue shift was observed along with 3.2 fold enhancement of acceptor emission intensity at 350 nm excitation. Furthermore, the emission due to the donor component was quenched as a result of the strong energy transfer from donor to acceptor. The almost complete energy transfer using 45mol% acceptor is also obvious from the inset photograph of dispersion of nanoparticles under UV lamp (366 nm) showing only green colour (Figure 5b).

The third bi-polymer nanoparticles design involves a novel core-shell nanoparticles prepared sequentially. Here, the donor forms the core which is coated with 45 mol% of acceptor (Figure 5c). Excitation of DA45 nanoparticles at donor excitation resulted in 19 nm blue-shift of the emission of the acceptor. The blue-shift is attributed to an increased D-A interactions. The increased oscillating dipole-dipole interactions upon excitation of donor create a nearby electric field, which does not allow the acceptor molecules to find their minima for relaxation so that PFBT-P moieties emit at higher energies.¹⁷ Furthermore, an efficient energy transfer leading to 10 fold enhancement of acceptor emission was observed at donor excitation. The incomplete energy transfer maintain a balance between the emission of both donor and acceptor components leading to white emission as can be seen in the inset photograph of DA45 nanoparticles.

Similarly, in the fourth nanoparticles design where the acceptor forms the core surrounded by donor polymer (Figure 5d), a 21 nm blue-shift in the acceptor emission was observed as noticed in the opposite design. However, the emission of the acceptor was enhanced by 11 fold with white-green emission colour. The slightly higher emission intensity of the acceptor is due to efficient energy transfer. Since the acceptor forms the core of the nanoparticles, loss of energy through reflection and other non-radiative means is negligible.

In the case of nanoparticles prepared without using Cu(I) catalyst for 1,3-dipolar cycloaddition, there was no significant differences in size as par those prepared using catalyst (ESI, Table S1, Fig. S7). However, some variations in optical properties were observed. In fact higher FRET efficiencies were invariably observed in uncatalyzed nanoparticles (ESI, Fig. S9-S11, Table S2).

The decay curves of catalyzed nanoparticles show shorter decay lifetime for the donor at 420 nm as compare to that of only the donor nanoparticles and also longer decay lifetime for the acceptor emission at 535 nm as compare to that of the acceptor alone (Figure 6a and b). These further illustrate the energy transfer between donor and acceptor. Similar trend of decrease in lifetime at 420 nm and increase in lifetime at 535 nm was observed for catalyst-free nanoparticles (Figure 6c and d). In fact the lifetimes at 535 nm for catalyst-free nanoparticles are longer than in the case of catalyzed nanoparticles; which are in agreement with steady-state PL results suggesting an enhanced FRET for the catalyst-free nanoparticles.

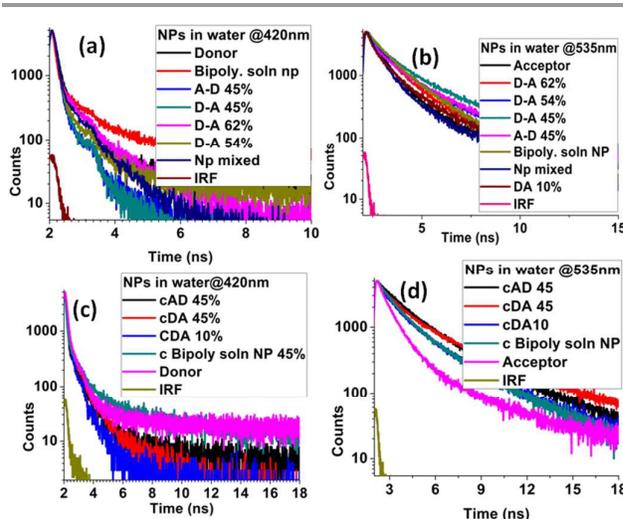


Fig.6 Biexponentially fitted decay curves of bipolymer nanoparticles (a) Fluorescence life-time decay curves of catalyzed Nanoparticles at 420 nm, (b) At 535 nm (c) Fluorescence life-time decay curves of catalyst-free Nanoparticles at 420 nm (d) At 535 nm

The fluorescence lifetimes of the nanoparticles reveal quantitative measurement of the energy transfer efficiency. The average lifetime of donor nanoparticles dispersion in water was found to be 0.162 ns while acceptor nanoparticles was 1.079 ns. Using equation (1), the energy transfer efficiencies were calculated and the results were tabulated in Table S2 (ESI).

$$\eta = 1 - \frac{\tau_{DA}}{\tau_D} \quad \text{Eq. (1)}$$

Where η denote energy transfer efficiency, τ_{DA} and τ_D denotes the averages lifetimes of donor in the presence and absence of acceptor respectively.

However, the energy transfer efficiency of NP mixed was not calculated using equation 1, because the donor-acceptor pairs are randomly moving in solution with no fixed distance. Nonetheless, all the other nanoparticles bound by a fixed distance could be evaluated using Eq. 1. DA62 which contains 62mol% acceptor as the shell shows the highest energy transfer efficiency of 73.45%. The high energy transfer efficiency of DA62 is due to high acceptor concentration which leads to complete energy transfer from the low content donor core. As for DA45 and cDA45 representing catalyzed bi-polymer nanoparticles and catalyst-free nanoparticles respectively, the difference in energy transfer efficiencies is in agreement with steady-state fluorescence results. The efficiencies of DA45 and cDA45 are 39.5% and 62.4% respectively. Again the lower energy transfer efficiency of DA45 compare to cDA45 was due to the quenching effect of copper sulfate used as a catalyst during nanoparticles preparation. Quenching by catalyst was more pronounced in the nanoparticles design where solutions of donor and acceptor were mixed before nanoparticles were prepared. For example a catalyst-free c.Soln nanoparticle has an efficiency of 64.8% while catalyzed Soln NP is 23.5%. The high quenching in this particular case can be understood from

the efficient mixing and distribution of the catalyst throughout the bi-polymer nanoparticles.

For possible application of these bi-polymer nanoparticles in solid state lighting, they should show energy transfer in the solid state as well. Thin film of bi-polymer nanoparticle was prepared on quartz surface by drop casting. Interestingly, all the bi-polymer nanoparticles exhibited high level of energy transfer comparable to those in nanoparticles dispersion in water (Figure 7). For NP mixed, where nanoparticles are prepared separately from donor and acceptor and then mix physically, very low energy transfer was observed. This result confirms that even at high concentration of physical mixture of donor and acceptor, they might not be at a favourable distance or orientation for energy transfer to take place. Also, limited exciton diffusion might lead to this observation.

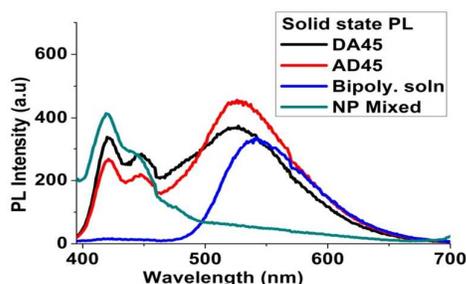


Fig. 7 Solid state photoluminescence of bi-polymer NPs. (λ_{ex} =350 nm).

In order to understand the effect of click reaction on the shape and morphology of bi-polymer nanoparticles, sequentially formed nanoparticles were prepared from bromide-functionalized polymers (PFB-Br and PFBT-Br, as donor and acceptor, respectively) as a control experiment. When compared with azide/alkyne-functionalized polymers which undergo click reaction to form stable nanoparticles, interesting differences in optical properties and morphology were observed. According to DLS and SEM data (ESI, Figure S12), when bi-polymer nanoparticles are prepared by click reaction (ADN3), they tend to exhibit smaller, monodispersed and more compact nanoparticles than the nanoparticles prepared from bromide-functionalized polymers (ADBr). Despite the small size differences; ADN3 is 106 nm while ADBr is 115 nm, the SEM micrographs showed that ADN3 nanoparticles are more monodispersed.

The optical properties ADN3 and ADBr were compared in Figure 8. Because of the compact nature of ADN3 nanoparticles which provides a favourable D-A distance for energy transfer, ADN3 demonstrated higher energy transfer than ADBr. Both nanoparticles emits at 420 nm and 520 nm. The emission at 520 nm was 24 nm blue shifted, compared to acceptor alone.

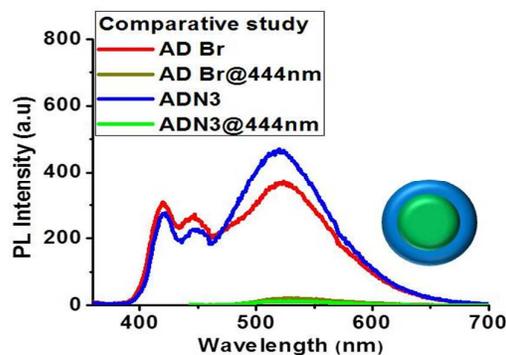


Fig. 8 Photoluminescence spectra of bi-polymer NPs (ADN3) prepared through click reaction and ADBr prepared from non-functionalized polymers. λ_{ex} =350 nm (red and blue lines) and 444 nm (dark and light green lines).

To demonstrate further that the nanoparticles are stabilized by cross-linking; water dispersions of bi-polymer nanoparticles prepared through click reaction (AD N3) and prepared from non-clickable polymers (ADBr) were evaporated to dryness under reduced pressure. The remaining residues were redispersed in THF and SEM images were taken. While nanoparticles of ADBr were disintegrated into polymer chains upon treating with THF and the SEM images showing no nanoparticles, SEM micrograph of ADN3 nanoparticles exposed to THF (ESI, Figure S13) revealed the presence of nanoparticles indicating that nanoparticles were not de-folded into separate polymer chains. Their size, however, enlarged from 99 nm in water to 300 nm in THF. Moreover, their energy transfer efficiency when they are redispersed in THF falls drastically to an unprecedented low level (ESI, Table S2). This can be attributed to the swelling of the nanoparticles in THF which is a good solvent, hence, putting the donor and acceptor at an unfavourable distance for efficient FRET to occur. Interestingly, the low energy transfer observed in solution of bi-polymer nanoparticles in THF which does not occur at all in the case of solution of ADBr nanoparticles or bare donor and acceptor polymers in THF suggested that the bi-polymer nanoparticles are covalently bound through click reaction. The triazole rings cross-linking donor and acceptor nanoparticles ensure that even when the nanoparticles are in good solvents (i.e. THF), they only swell to certain degree but do not disintegrate into their respective polymer chains. Despite the morphology of the bi-polymer nanoparticles in THF are nanoparticle-like, their emission wavelengths shifted to the emission wavelength of the corresponding polymers in THF. The emission of nanoparticles shifted from 420 nm and 544 nm to 407 nm and 535 nm of polymer chain respectively. We have also evaporated THF and re-dispersed the nanoparticles in water once again. The re-dispersed nanoparticles were compared with nanoparticles prepared from non-clickable polymers (ADBr NP). All the nanoparticles dispersions in water that were cross-linked through click reaction (both for catalyzed and uncatalyzed) show restoration of energy transfer. However, the energy transfer in ADBr nanoparticles was not fully restored (Figure S13).

White-emitting Tandem Nanoparticles

Although we have achieved to obtain white emission from the bi-polymer core-shell type nanoparticles by tuning the ratio of blue and green emitting polymers, the white colour quality was not at the desirable level. Therefore, in order to generate high quality white light emission, tri-layered or we call tandem nanoparticles, were designed from three polymers (Figure 9) using four nanostructured design methods as we discussed for bi-polymer nanostructures. In the first method, 'NPs Mixed' was design by preparing nanoparticles from each of the three polymers separately and then mixing them in certain ratio. In the second method, 'T Sol NP' was prepared by mixing solution of the three polymers in THF and then nanoparticles were made from the resulting solution. In the third and fourth methods, sequentially formed nanoparticles were prepared; nanoparticles of one polymer are first prepared, followed by coating with the second polymer. The resulting bi-polymer nanoparticles are further coated with the third polymer to obtain sequentially formed tandem nanoparticles.

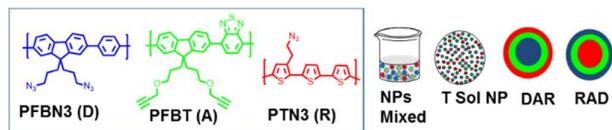


Fig. 9 Schematic representation of tandem nanostructure designs

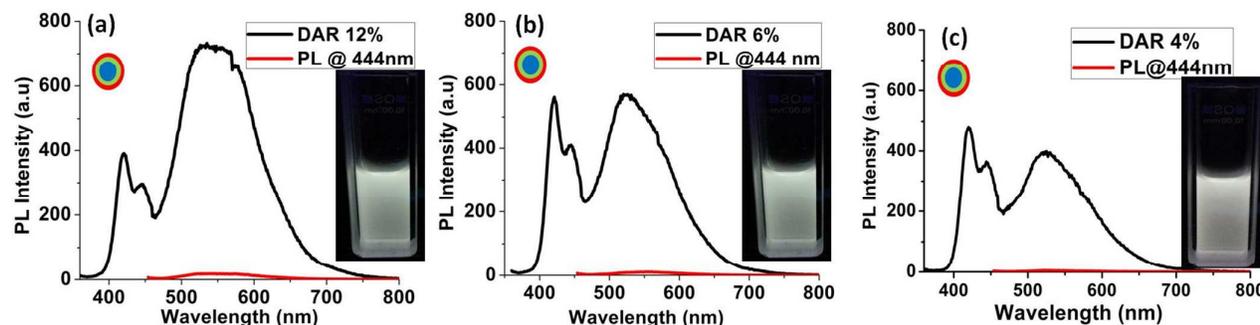


Fig. 11 Emission spectra of (a) DAR 12% NPs (λ_{ex} =350 nm); (b) DAR 6% NPs and (c) DAR 4% (λ_{ex} =350 nm). The red lines represent the excitation at 444 nm.

In the first method, 'NPs mixed' show emission spectrum similar to the individual nanoparticles. Some energy transfer from blue to green and then to red polymer could be observed. However, the energy transfer was inefficient owing to the large distance of the nanoparticles in solution. The dominance of the donor component at 420 nm results in blue colour. In the second designs, where solutions of three polymers were simultaneously used to prepare 'T Sol NPs', a complete energy transfer from donor to acceptor and finally to the red polymer was observed. This result is similar to those observed in the bi-polymer nanoparticles mentioned earlier. All the blue and green polymer components of the spectrum at 420 nm and 535 nm respectively have been transferred to the red polymer component at 595 nm. The emission of the red polymer was

enhanced 3 fold through energy transfer compare to the emission of the red polymer at its excitation wavelength. In the third design denoted DAR NPs, blue polymer nanoparticles was coated with green polymer followed by red polymer. DAR NPs show high energy transfer to the green polymer component with 10 nm blue shift. The emission intensity of the blue polymer component at 420 nm was very low due to the efficient energy transfer to acceptors. The emission intensity of the green polymer was 8 times higher at 350 nm excitation than its own excitation at 444 nm. Finally, for the fourth design denoted by RAD NP, red polymer nanoparticles were coated with green polymer followed by blue polymer. Formation of sequentially formed tandem nanoparticles was evidenced from the spectral changes.

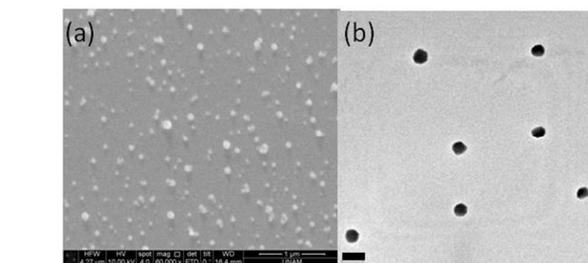


Fig. 10 Size and morphology of DAR 4% NPs \sim 101nm (a) SEM micrograph (scale 1 μ m) and (b) TEM micrograph (scale 0.2 μ m)

The energy transfer study of the four tandem nanoparticles designs are presented in Figure S17 (ESI). Each of the tandem nanoparticles contain equal ratio of blue, green and red polymer for comparison. They all contain 58 W% blue, 24 W% green and 18 W% red polymers.

The distinct emission of the three polymers can be seen at the 350 nm excitation wavelength. However, the emission intensities of blue and green polymers are very low compare to the red polymer due to energy transfer. Furthermore, the emission of the red polymer was 35 nm blue-shifted compare to polythiophene nanoparticles alone. In addition, the emission intensity of the red polymer component of RAD NPs is 6.6 times higher than the emission intensity of red polymer nanoparticles at its own excitation wavelength. Such amplified emission is attributed to high energy transfer and prevention of aggregated quenching of the red polymer when doped with other polymers.

Among the four nanostructured designs studied, DAR shows emission colour that resembles white light. As a result DAR NP design was adapted to prepare a set of tandem white emitting nanoparticles. To further tune the emission of DAR, the 42 W% green and red emitting polymers components was limited to 12 W% to obtain a new white emitting tandem nanoparticles denoted DAR12%. DAR 12% was prepared with 88 W% blue, 9 W% green and 3 W% red polymers. The green and red polymers in DAR12% add up to 12% by weight. In Figure 11a, the emission spectrum of DAR 12% showed the distinct emissions of the three polymers. Due to incomplete energy transfer and wide coverage of the visible region, white emission was achieved.

Moreover, the emission of DAR 12% NP was also tuned by further limiting the green and red polymer components to give DAR 6% and DAR 4% NPs. Reduction of the blue and green polymer components from 12% to 4% by weight is expected to induce incomplete energy transfer and hence generation of white emission. In DAR 6%, the compositions of polymers are 94 W% blue, 4.5 W% green and 1.5 W% red polymers. For DAR 4% where the compositions are 96 W% blue, 3 W% green and 1 W% red polymer, the white emission was comparable to that of DAR 6% NPs (Figure 11b). The quality of white emission from DAR 4% was the best achieved (Figure 11c). The average size of DAR 4% NPs was determined to be 101nm according to DLS measurements.

The fluorescence decay curves of tandem nanoparticles at 420 nm show that NPs mixed has longer lifetime (0.158 ns) compare to other tandem nanoparticles designs which ranges from 0.048-0.126 ns. This indicates an inefficient energy transfer

in nanoparticles mixed. Furthermore, the fluorescence decay curves at 535 nm (Figure 12b) illustrate energy transfer in the tandem nanoparticles except for NPs mixed which has the shortest lifetime at 535 nm (ESI, Table S3).

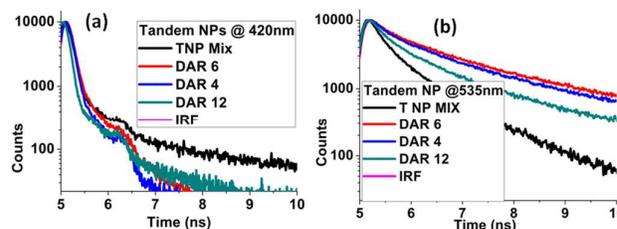


Fig. 12 Biexponentially fitted decay curves of tandem nanoparticles (a) Fluorescence life-time decay curves of tandem NPs at 420 nm, (b) At 535 nm

To realize proof-of-concept white light - emitting diode (LED) employing tandem nanoparticles, the first step has been the evaluation of the colour quality of tandem nanoparticle dispersions. Our calculations revealed that DAR4% dispersion exhibits the best colour rendering index (CRI) reaching 58.3 and colour quality scale (CQS) reaching 74.1, which indicate the capability of the light source to render the real colours of the objects, along with a reasonable correlated colour temperature (CCT) of 8716 K.

Subsequent to the selection of the tandem nanoparticles for white LED application, tandem nanoparticle films were prepared by dissolving 120 mg of poly(vinyl)pyrrolidone in 2 mL of nanoparticle dispersion. Later, 0.7 mL of this mixture was drop-casted on glass and dried at ca. 60 °C. Finally, the prepared film was placed on top of a LED emitting at 380 nm and the emission spectrum was recorded using a Maya 2000 spectrometer at varying current levels. Corresponding emission spectra were presented in Figure 13 together with the corresponding CRI, CQS, CCTs and corresponding Commission Internationale de L'Eclairage (CIE) coordinates (full coordinates were given in the ESI, Table S4).

This LED exhibited CCTs between 4910 and 4952 K, which falls in the region of frequently used white light sources. Additionally, the CRI values varied between 71.9 and 72.4, and CQS values varied between 78.4 and 79.0 at varying applied currents. We observe that higher photon flux from the LED chip at higher currents does not cause any significant change in the colour quality of the final device.

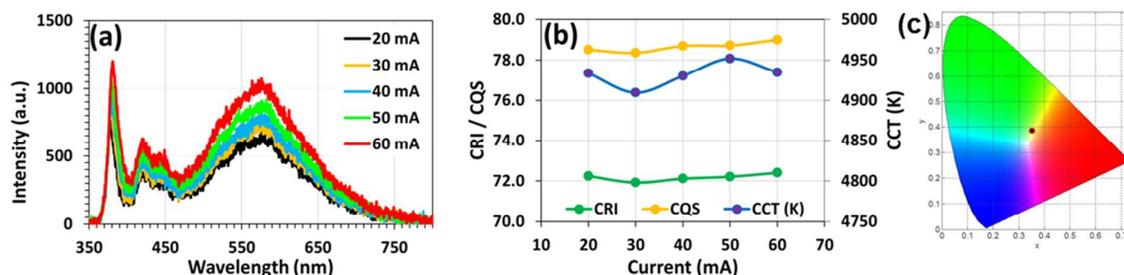


Fig. 13 (a) The spectra and (b) CRI, CQS, and CCT of the tandem nanoparticle integrated white LED at varying current levels and (c) corresponding CIE coordinates.

The colour rendition performance of this nanoparticles integrated LED becomes comparable with YAG phosphor integrated LEDs.

DAR 4% nanoparticle using Cu (I)-catalyst integrated LEDs were also prepared following the same procedure as the DAR 4% (without using catalyst) tandem white nanoparticles. These LEDs exhibited inferior colour rendering performance compared to DAR 4% white nanoparticle LEDs (Fig.S18). This is mainly because of the lower intensity of the blue part in the spectrum compared to the previous case. This variation in the spectrum mainly occurs due to the presence of the Cu ions causing quenching. This lower intensity also affects the perceived colour to a greenish shade while DAR 4% is much closer to the white point on the chromaticity diagram (Fig.S19).

Experimental

All experimental details regarding the synthesis and characterization of polymers and nanoparticles were provided in the supporting information section.

Conclusions

Four nanoparticle designs were utilized in this work. The first approach involved preparing PFBN3 and PFBT nanoparticles separately and mixing them at a determined ratio. In the second approach, solutions of PFBN3 and PFBT are mixed before nanoparticle formation; the nanoparticles are prepared from mixture of the two polymer solution. In third and fourth approach, sequentially formed nanoparticles were designed. These designs, especially the third one in which the core is made out of donor and the shell is composed of acceptor polymers, found to be most efficient one allowing us to tune the emission colour and the quality of the white light by adjusting the nanoparticles composition and the energy transfer. Using this approach, we were able to prepare bi-layered and tri-layered core-shell type nanoparticles by clicking polymers with appropriate functional groups through alkyne-azide 1,3-dipolar cycloaddition to obtain stable and shape persistent nanoparticles that remained intact in different solvents because of the cross-linking of functional groups through click chemistry. Interestingly, even in the absence of Cu(I)-catalyst alkyne-azide 1,3-dipolar cycloaddition took place because of the proper alignments of the alkyne-azide functional groups in these nanoparticles.

Although bi-layered polymer nanoparticles were capable to produce white emission, tri-layered polymer nanoparticles or tandem nanoparticles turned out to be displaying better white light qualities due to its wider coverage of the spectrum. Moreover, LEDs fabricated using tandem nanoparticles in the absence of Cu(I)-catalyst exhibited superior colour rendering performance compared to the one prepared from Cu(I)-catalyzed nanoparticles.

These tandem nanoparticles can be used as colour converters to realize a white LED acquiring a colour quality comparable to existing phosphor based white light emitting diodes.

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Table of Contents

A series of blue, green and red emitting polymers that are appropriately functionalized with alkyne and azide functional groups have been prepared and clicked together to construct of bi-layered and tri-layered white emitting core-shell type nanoparticles.

