

Electronic Supplementary Material (ESI)

Construction of multi-layered white emitting core-shell type nanoparticles by clicking light emitting polymers

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Experimental section

All the reagents utilized in the experiments were purchased from Sigma-Aldrich Chemical Co. and were used as received. The purification of monomers were done using column chromatography loaded with silica gel (Kieselgel 60, 0.063-0.200 mm) and thin layer chromatography (TLC) decorated with silica gel (Kieselgel F254, 1 mm) to monitor separation of side products. Morphological characterization was achieved by transmission electron microscopy (TEM, FEI Tecnai G2 F30) and scanning electron microscopy (SEM). The size of the nanoparticles was measured by dynamic light scattering (DLS, Zetasizer Nano-ZS). Measurements were carried out at 633 nm and the laser, as the light source, was used at room temperature. The time dependent autocorrelation function of the scattered light intensity was measured at an angle

of 90°. The average particle diameter was calculated by the Marquardt method. The DLS measurements were usually repeated at least three times and the average values are reported. For the optical characterization, a UV–vis spectrophotometer (Cary UV–vis) and a fluorescence spectrophotometer (Cary Eclipse Fluorescent spectrophotometer) equipped with a xenon lamp as the excitation source were used. For the structural characterization, nuclear magnetic resonance (NMR, a Bruker Avance III 400 for ^1H and a 100 MHz spectrometer for ^{13}C) and FT-IR (Bruker TENSOR 27) spectra were obtained. The molecular weight of the polymers were determined using gel permeation chromatography (GPC) on Polymer Laboratories PL-GPC220 system equipped with a RI detector in THF using a calibration curve of polystyrene standards. The photophysical properties of nanoparticles including bi-polymer and tandem nanoparticles were investigated using Time-resolved fluorescence spectroscopy (PicoQuant, FluroTime200) equipped with Time-correlated single photon counting (TCSPC) electronics which is capable of detecting picoseconds and slower lifetime values. Deionized water was used to prepare the nanoparticles.

Synthesis:

Synthesis of 2,7-dibromo-9,9-bis(3-bromopropyl)-9*H*-fluorene,^{1,2} 2-(2,5-dibromothiophen-3-yl)ethanol,³ poly[9,9-bis(3-bromopropyl)-9*H*-fluorene-co-benzene],⁴ PFBBr, poly[4-(9,9-bis(3-bromopropyl)-9*H*-fluoren-7-yl)-co-(1,4-benzo-{2,1,3}-thiadiazole)]^{1,2,5} have reported in our previous publications.

Synthesis of poly[(9,9-bis{3-azidopropyl}fluorenyl-2,7-diyl)-co-benzene] (PFBN3)

Poly [9,9-bis(3-bromopropyl)-9*H*-fluorene-co-benzene] (200 mg, 0.357 mmol) and NaN_3 (1.07 mmol, 70.0 mg) was dissolved in degassed DMF (15 mL) and then the reaction mixture was heated up to 50-60 °C for 24 hours while stirring. After the completion of reaction, the solvent was completely evaporated by rotary evaporator. The crude product was washed with water thoroughly. The precipitate was dissolved in minimum amount of THF and precipitated into cold methanol, the precipitated pure polymer was filtered and dried under vacuum for 12 h. Yield: 105 mg, 60%. IR (Solid state, KBr): ν (cm^{-1}): 3030, 1598 (aromatic), 2919, 1458, 1262 (alkyl), 2098

(azide). $^1\text{H-NMR}$ (400MHz, CDCl_3 , 25°C): δ 0.98-1.78 (m, 4H), 2.18-2.36 (m, 4H), 3.02-3.17 (m, 4H), 7.40-7.95 (m, aromatic, 10H).

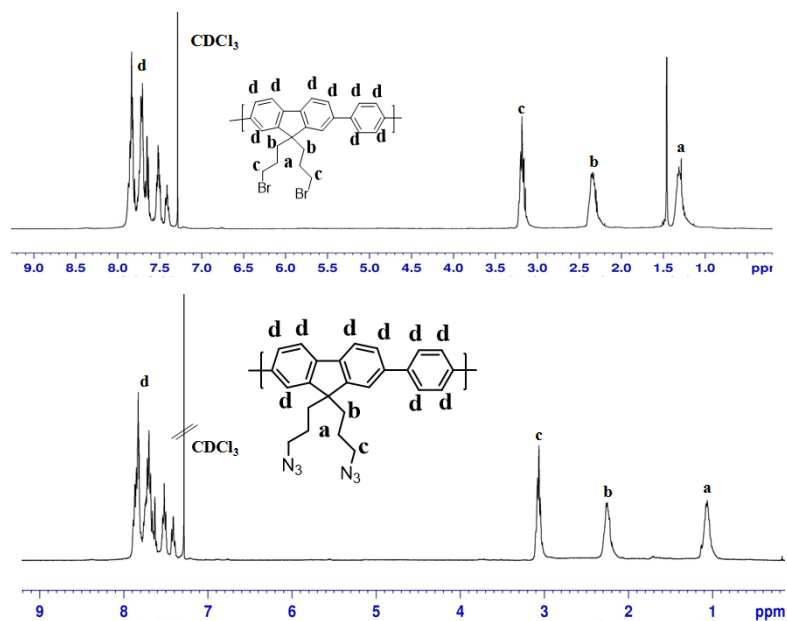


Fig. S1 ^1H NMR spectra of poly[9,9-bis(3-bromopropyl)-9H-fluorene-co-benzene], poly [9,9-bis(3-azidopropyl)-9H-fluorene-co-benzene](PFB-N3), (CDCl_3 , 400 MHz, 25°C)

Synthesis of poly[(9,9-bis(3-(prop-2-ynoxy)propyl)fluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1,3}-thiadiazole)] (PFBT-P)

Poly[4-(9,9-bis(3-bromopropyl)-9H-fluorenyl-7-yl)-co-(1,4-benzo-{2,1,3}-thiadiazole)] PFBT-Br (250 mg, 0.461 mmol) was dissolved in DMF (8 mL). K_2CO_3 (5eq) was added to excess propargyl alcohol (3 mL) in a two-neck flask and stirred for 30 min. PFBT-Br solution was then injected into the reaction flask and stirred at room temperature for 48 h. Yield: 77%. IR (Solid state, KBr): ν (cm^{-1}): 3300, ($\equiv\text{C-H}$ stretch), 2119 ($\text{C}\equiv\text{C}$ stretch), 2926 ($-\text{C-H}$ stretch) 1727 ($-\text{C-N}$ stretch). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ 1.31 (m, 4H, $-\text{CH}_2$), 1.87 (m, 4H, $-\text{CH}_2$), 2.32 (s, 1H, $\equiv\text{CH}$), 3.41 (m, 2H, $-\text{CH}_2$), 4.00 (m, 2H, $-\text{CH}_2$), 7.40-8.00 (m, 8H, aromatic).

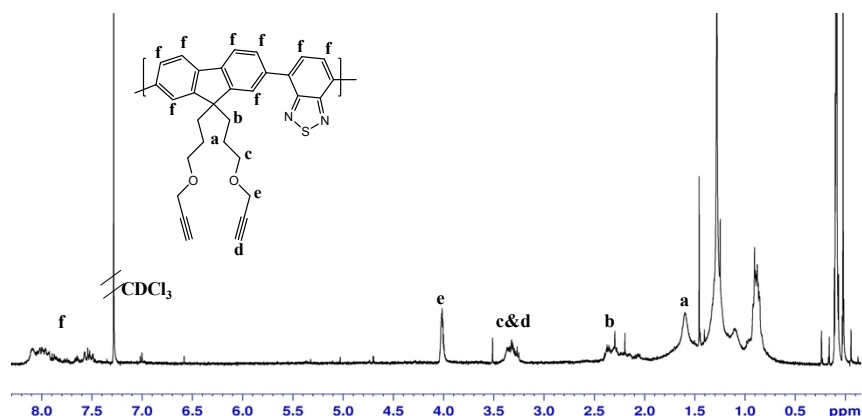
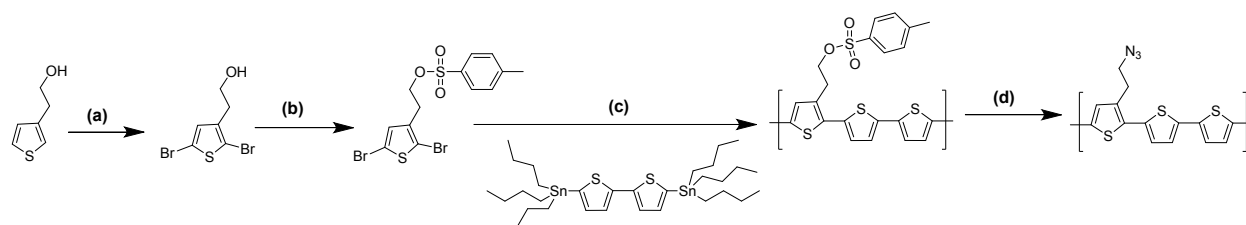


Fig. S2 ^1H NMR spectrum of poly[(9,9-bis(3-(prop-2-ynoxy)propyl)fluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1,3}-thiadiazole)](PFBT) (CDCl_3 , 400 MHz, RT).

Synthesis and characterization of poly[(2-azidoethyl)-2-(5-(thiophen-2-yl)thiophen-2-yl)thiophene (PTN3)



Scheme S1. Reaction scheme for **PTN3**. (a) 2-(thiophen-3-yl)ethanol, NBS, EtOAc, 25 °C, 12 h, 60% (b) Toluenesulfonyl chloride, CH_2Cl_2 , pyridine, 0 °C, 3 h, 90% (c) THF/DMF (1:1, v/v), $\text{Pd}(\text{Ph}_3)_4$, 90 °C, 72 h, 46% (d) NaN_3 , DMF, 25 °C, 72 h, 75%.

Synthesis of 2-(2,5-dibromothiophen-3-yl)ethyl-4-methylbenzenesulfonate

2-(2,5-dibromothiophen-3-yl)ethanol (1.000 g, 3.496 mmol) was dissolved in 5 mL dry CH_2Cl_2 and toluenesulfonyl chloride (0.999 mg, 5.244 mmol) was added and followed by pyridine (0.6 mL). The mixture was stirred at 0 °C for 3 h. After the reaction was over, the mixture was diluted with CH_2Cl_2 and washed consecutively with water, 1 M HCl, sat. NaHCO_3 (aq) and brine solution. Collected organic phase was dried over Na_2SO_4 . Solvent was removed under reduced

pressure and the residue was purified through Si- column chromatography using the mixture of cyclohexane/ethyl acetate. Yield: 1.4 g, 90%.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ 2.47 (3H, s, CH_3 -), 2.88 (2H, t, $^3\text{J} = 6.4$ Hz, $-\text{CH}_2-$), 4.18 (2H, t, $^3\text{J} = 6.4$ Hz, $-\text{CH}_2-$), 6.70 (1H, s, thiophene), 7.33 (2H, d, $^3\text{J} = 8.0$ Hz, phenyl), 7.72 (2H, d, $^3\text{J} = 7.2$ Hz, phenyl).

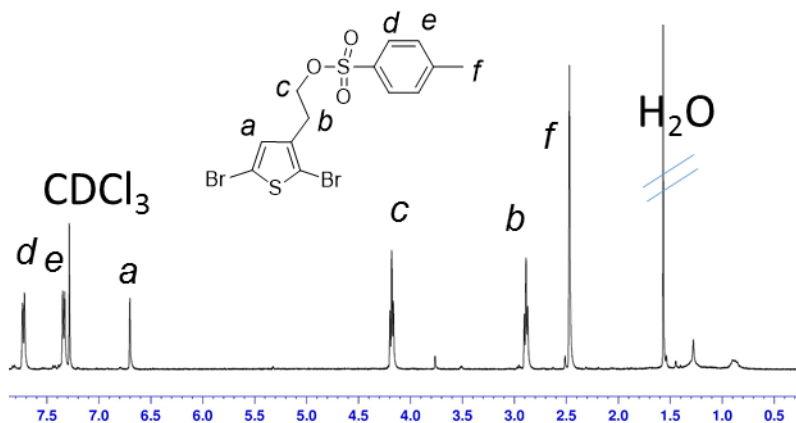


Fig. S3 ^1H NMR spectrum of 2-(2,5-dibromothiophen-3-yl)ethyl-4-methylbenzenesulfonate, (CDCl_3 , 400 MHz, 25°C)

Poly[(thiophen-2-yl)thiophen-2-yl)-3-(2-tosylethyl)thiophene], PTH-Ts

2-(2,5-dibromothiophen-3-yl)ethyl-4-methylbenzenesulfonate (1.2569 g, 2.8553 mmol) and 5,5'-bis(tributylstannyl)-2,2'-bithiophene (2.1253 g, 2.8553 mmol) were placed into a two-necked round bottomed flask; dry THF (15 mL) and dry DMF (15 mL) were added under argon and then the reaction mixture was subjected to 3 freeze-pump-thaw cycle to remove oxygen. Then a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ (160 mg, 0.14 mmol) was added and the reaction mixture was heated up to 90°C for 48h while stirring. After the completion of reaction, the solvent was completely evaporated by rotary evaporator. The crude product was washed thoroughly with water to remove the impurities and the precipitate was dissolved in minimum amount of THF and precipitated into cold methanol. The precipitates were collected and redissolved in THF and precipitated into cold methanol. The precipitation was repeated several times. The precipitates were collected and dried under vacuum for 12 h. Yield: 600 mg, 48%.

Gel-permeation chromatography (GPC): $M_n = 20747 \text{ g mol}^{-1}$, $M_w = 23015 \text{ g mol}^{-1}$ (Polystyrene as standard).

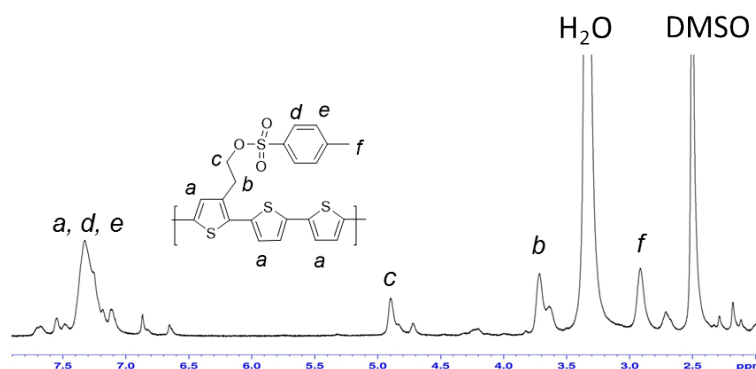


Fig. S4 ¹H NMR spectrum of Poly[(thiophen-2-yl)thiophen-2-yl]-3-(2-tosylethyl)thiophene], PTH-Ts, (d₆-DMSO, 400 MHz, 25 °C).

Synthesis and characterization of poly[(2-azidoethyl)-2-(5-(thiophen-2-yl)thiophen-2-yl)thiophene (PTH-N3)

Poly[(thiophen-2-yl)thiophen-2-yl]-3-(2-tosylethyl)thiophene, PTH-Ts (100 mg, 0.232 mmol) and NaN₃ (23 mg, 0.35 mmol,) was dissolved in degassed DMF (15 mL) and then the reaction mixture was sonicated for a while and allowed to stir at 25 °C for 72 h. After the completion of reaction, the solvent was completely evaporated by rotary evaporator. The crude product was washed with water thoroughly. The precipitate was dissolved in minimum amount of THF and precipitated in water, the precipitated pure polymer was filtered and dried. Yield: 53 mg, 75%. IR (Solid state, KBr): ν (cm⁻¹): 3030, (aromatic), 2919, 2848 (-CH stretching), 2098 (azide). ¹H-NMR (400 MHz, CDCl₃, 25°C): 1.78-2.00 (m, 2H), 2.98-(m, 2H), 7.40-7.95 (m, aromatic, 6H).

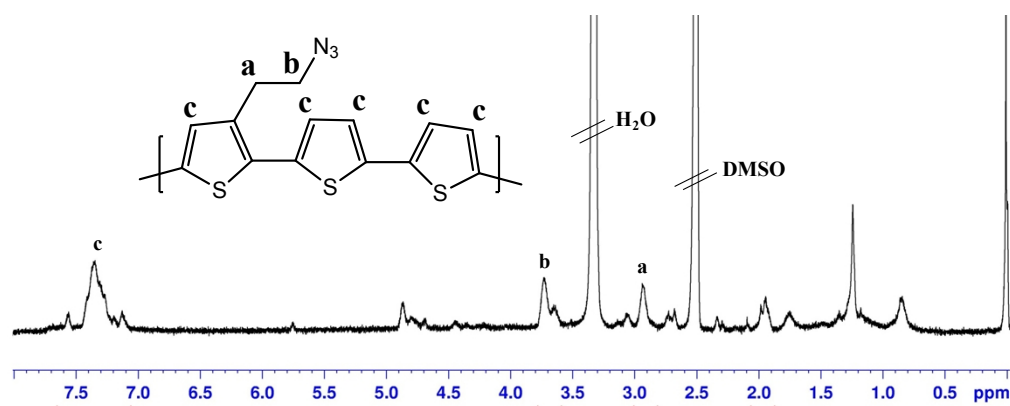


Fig. S1 ^1H NMR spectrum of poly[(2-azidoethyl)-2-(5-(thiophen-2-yl)thiophen-2-yl)thiophene] (d_6 -DMSO, 400 MHz, 25 °C)

Preparation of nanoparticles:

Synthesis and characterization of PFB-N3 NPs

0.25 mg of PTB-N3 was dissolved in 2 mL THF and ultrasonicated for 10 min. The solution was then filtered through 0.45 μm syringe filter and injected into 20 mL of Milli-Q water (18.2 M Ω) and ultrasonicated for 40 min. THF was removed by vacuum evaporator at 40 °C to obtain stable NPs. Characterization of NPs was done by UV-Vis spectroscopy, fluorescence spectroscopy, DLS (Zeta sizer), SEM and TEM.

Synthesis and characterization of PFBT-P NPs

0.25 mg of PFBT-P was dissolved in 2 mL THF and ultrasonicated for 10 min. The solution was then filtered through 0.45 μm syringe filter several times until clear solution was obtained. The clear solution was injected into 20 mL of Milli-Q water (18.2 M Ω) and ultrasonicated for 40 min. THF was removed by vacuum evaporator at 40 °C to obtain stable NPs. Characterization of NPs was done by UV-vis spectroscopy, fluorescence spectroscopy, DLS (Zeta sizer), SEM and TEM. All the results confirmed formation of stable NPs. However, the emission intensity decreased upon NP formation.

White-emitting bi-polymer nanoparticles

Four methods were used to design bi-polymer NP dispersion in water. PFB-N3 and PFBT-P were chosen because of the strong spectral overlap. The amount of donor in each sample was kept constant.

Method 1

0.5 mg of PFB-N3 polymer was dissolved in 2 mL THF and ultrasonicated for 10 min. The solution was then filtered through 0.45 μm syringe filter and injected into 20 mL of Milli-Q water (18.2 M Ω) and ultrasonicated for 40 min. THF was removed by vacuum evaporator at 40°C to obtain stable NPs. Similarly, 0.5 mg (45 mol%) PFBT-P polymer was used to prepare acceptor NPs. The two NPs were then mix and denoted NP mixed.

Method 2

0.5 mg PFB-N3 and 0.5 mg (45 mol%) PFBT-P were dissolved in 2 mL THF and ultrasonicated for 10 min. The solution was then filtered through 0.45 μm syringe filter and injected into 20 mL of Milli-Q water (18.2 M Ω) and ultrasonicated for 1hr. THF was removed by vacuum evaporator at 40 °C to obtain stable NPs. The resulting NPs was abbreviated as Soln NPs.

Method 3

In this design, bi-polymer NPs were formed sequentially. First, 0.5 mg of PFB-N3 (D) polymer was dissolved in 2 mL THF and ultrasonicated for 10min. The solution was then filtered through 0.45 μm syringe filter and injected into 20 mL of Milli-Q water (18.2 M Ω) and ultrasonicated for 40min. After 40 min of ultrasonication, a filtered solution of 0.5 mg (45 mol%) PFBT-P (A) in 2 mL THF was added into the preformed PFB-N3 NPs while ultrasonication. Ultrasonication was continued for another 40 min. THF was removed by vacuum evaporator at 40 °C to obtain stable NPs. The resulting bi-polymer NPs was denoted DA 45%, donor being core and surrounded with 45 mol% acceptor. Also DA 10% and DA 62% were prepared similarly with the same donor concentration (0.5 mg) but 10 mol% and 62 mol% of acceptor respectively.

Method 4

In this design, bi-polymer NPs were formed sequentially. First, 0.5 mg (45 mol %) of PFBT-P (A) polymer was dissolved in 2 mL THF and ultrasonicated for 10 min. The solution was then filtered through 0.45 μm syringe filter and injected into 20 mL of Milli-Q water (18.2 M Ω) and

ultrasonicated for 40 min. After 40 min. of ultrasonication, a filtered solution of 0.5 mg PFB-N3 (D) in 2 mL THF was added into the preformed PFBT-P NPs while ultrasonication. Ultrasonication was continued for another 40 min. THF was removed by vacuum evaporator at 40 °C to obtain stable NPs. The resulting bi-polymer NPs was denoted AD 45%, acceptor being core and surrounded with donor.

White-emitting tandem nanoparticles

White emitting tandem NPs were obtained using three polymers: PFB-N3, PFBT-P and PTH-N3 polymers. Four methods of nanostructured designs were prepared and investigated.

Method 1

0.5 mg PFB-N3, 0.25 mg PFBT-P and 0.12 mg PTH-N3 polymers were converted separately into their respective NP form by reprecipitation as described earlier. The resulting NPs of the three polymers were mixed physically and denoted NP Mixed.

Method 2

0.5 mg PFB-N3, 0.25 mg PFBT-P and 0.12 mg PTH-N3 polymers were dissolved in 2 mL THF and ultrasonicated for 10 min. The solution was then filtered through 0.45 µm syringe filter and injected into 20 mL of Milli-Q water (18.2 MΩ) and ultrasonicated for 1hr. THF was removed by vacuum evaporator at 40 °C to obtain stable NPs. The resulting NPs was denoted T.soln NPs.

Method 3

In this design, tandem NPs was formed sequentially. First, 0.5 mg of PFB-N3 (D) polymer was dissolved in 2 mL THF and ultrasonicated for 10min. The solution was then filtered through 0.45 µm syringe filter and injected into 20 mL of Milli-Q water (18.2 MΩ) and ultrasonicated for 40 min. After 40 min of ultrasonication, a filtered solution of 0.25 mg (24 mol%) PFBT-P (A) in 2 mL THF was added into the preformed PFB-N3 NPs while ultrasonication. Ultrasonication was continued for 30 min. Finally, 0.12 mg (18 mol %) PTH-N3 solution in 2 mL THF was also added to the preformed bi-polymer NPs and ultrasonicated for another 30 min. THF was removed by vacuum evaporator at 40 °C to obtain stable NPs. The resulting tandem NPs was denoted DAR. For DAR 12%, DAR 6% and DAR 4%, the amount of PFBN3 was constant while PFBT-P was

0.06 mg (9 mol %), 0.03 mg (4.5 mol %) and 0.2 mg (3 mol %) and PTN3 was 0.01 mg (2 mol %), 0.006 mg (1.5 mol %) and 0.0033 mg (1 mol %) respectively.

Method 4

This design is the reverse of the third method; here tandem NPs was also formed sequentially. First, 0.12 mg (18 mol %) PTN3 polymer was dissolved in 2 mL THF and ultrasonicated for 10 min. The solution was then filtered through 0.45 μm syringe filter and injected into 20 mL of Milli-Q water (18.2 M Ω) and ultrasonicated for 40 min. After 40 min of ultrasonication, a filtered solution of 0.25 mg (24 mol %) PFBT-P (A) in 2 mL THF was added into the preformed PTH-N3 NPs while ultrasonication. Ultrasonication was continued for 30 min. Finally, 0.5 mg PFB-N3 solution in 2 mL THF was also added to the preformed bi-polymer NPs and ultrasonicated for another 30 min. THF was removed by vacuum evaporator at 40 $^{\circ}\text{C}$ to obtain stable NPs. The resulting tandem NPs was denoted RAD.

Table S1 Summary of DLS data for polymer nanoparticles

	Size by DLS (nm)	SEM	TEM	PDI
PFB-N3-NP	64	✓	✓	0.190
PFBT-P-NP	63	✓	✓	0.216
PTH-N3-NP	80			0.272
Soln-NP (with catalyst)	74			0.245
D-A (with catalyst)	100	✓	✓	0.204
A-D (with catalyst)	97			0.166
cDA 45 (W/O catalyst)	99	✓		0.204
cAD (W/O catalyst)	102			0.253
DAR 12%	116	✓	✓	0.159
DAR 6%	115	✓	✓	0.185
DAR 4%	101	✓	✓	0.129

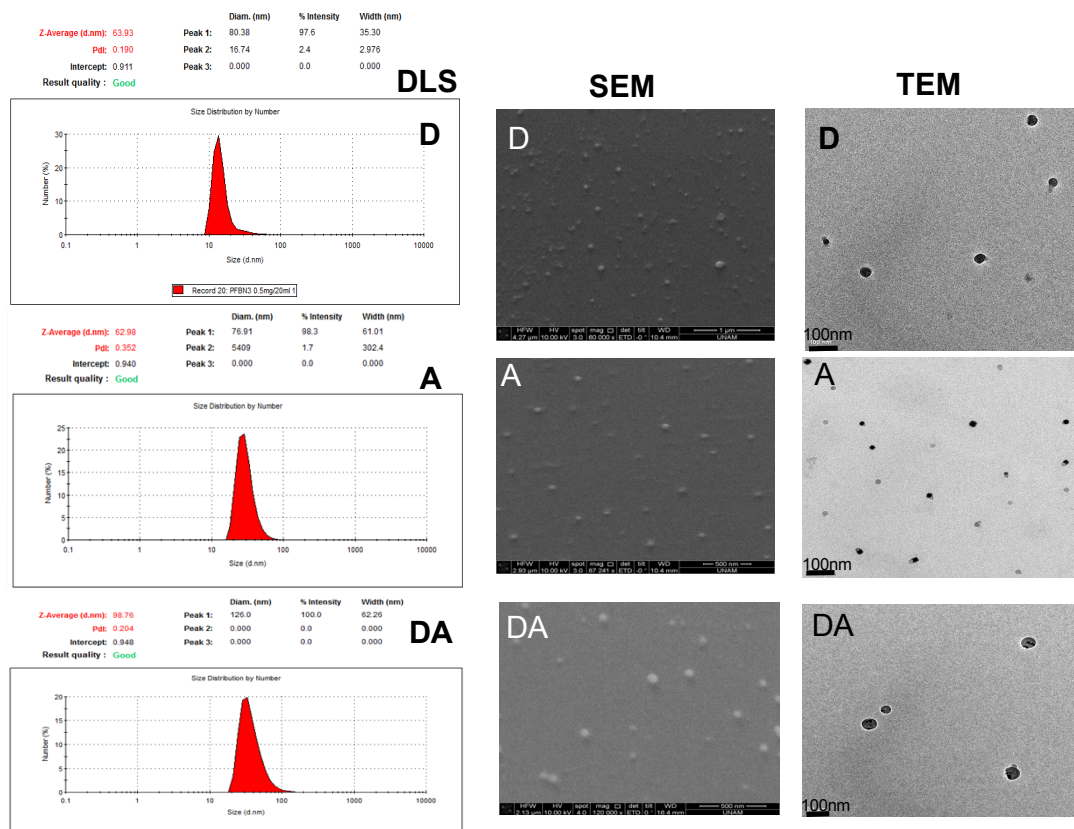


Fig. S2 DLS, SEM and TEM image of donor (PFB-N3), acceptor (PFBT-P) and bipolymer nanoparticles, design 3 (DA 45%)

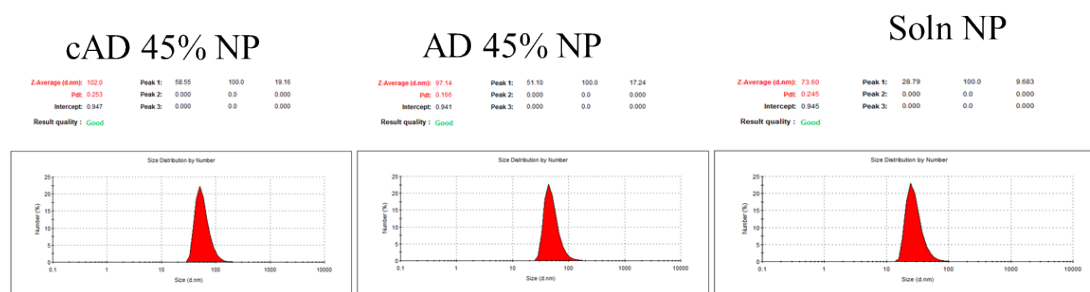


Fig. S7 DLS histograms of nanoparticles of cAD 45% NP prepared without catalyst; AD 45% NP prepared with catalyst; Soln NP prepared with catalyst Cu(I).

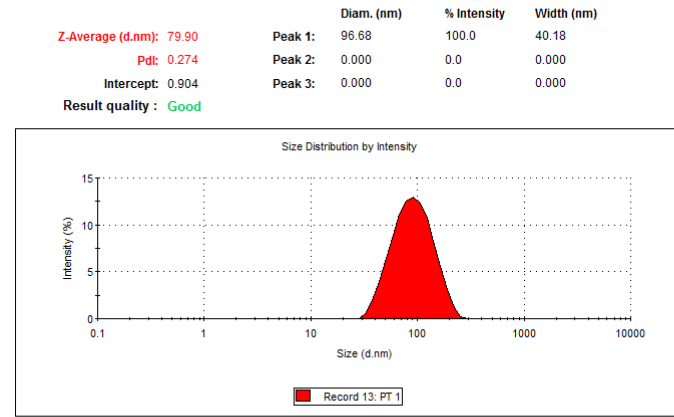


Fig. S8 DLS of polythiophene nanoparticles (PTN3)

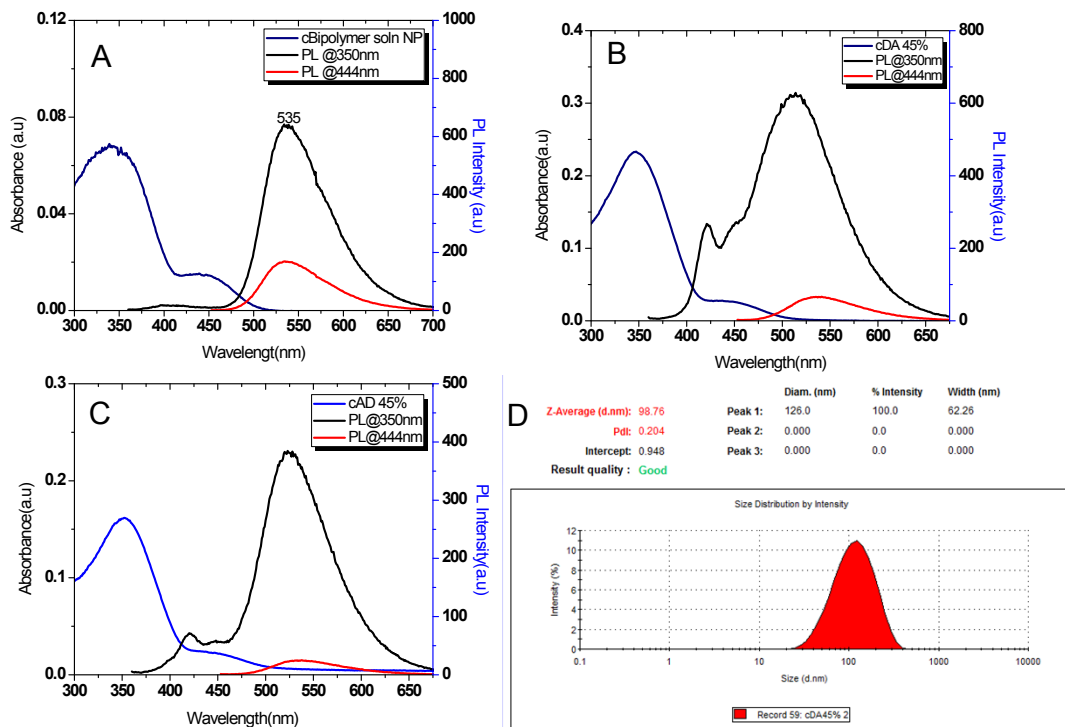


Fig. S9 Absorbance and emission spectra of catalyst free bi-polymer NPs (a) c-soln NP (NPs prepared from the solutions of PFB-N3+ PFBT-P without copper catalysts) (b) cDA 45 NPs (c) cAD 45 NPs (d)The size of cDA 45 NPs from DLS measurements (98.76nm)

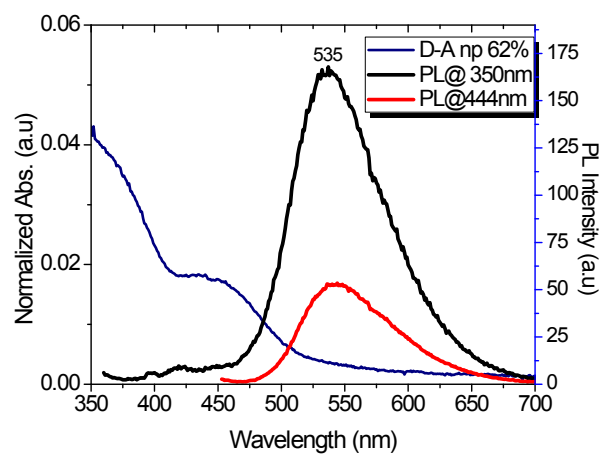


Fig. S10 Absorbance and emission spectra of DA 62 % NPs (Excitation at 350 nm).

Table S2: Fluorescence lifetime of NPs dispersion in water and in THF (intensity weighted)

S/N	NPs in Water	τ_{avr} [ns] @420nm	τ_{avr} [ns] @535nm	η [%]	NPs in THF	τ_{avr} [ns] @410nm	τ_{avr} [ns] @535nm	η [%]
1	DA 45	0.098	1.516	39.51	DA 45	0.583	1.04	4.43
2	cDA 45	0.061	2.130	62.35	cDA 45	0.560	1.57	8.20
3	AD 45	0.082	1.229	49.38	AD 45	0.558	1.91	8.52
4	cAD 45	0.073	2.110	54.94	cAD 45	0.585	1.81	4.10
5	Soln NP	0.124	1.300	23.45	Soln NP	0.501	1.53	17.87
6	C.Soln NP	0.057	1.560	64.81	C .Soln NP	0.608	1.82	0.33
7	NP mixed	0.044	0.826	-	NP mixed	0.530	1.23	-
8	DA 10	0.090	1.000	44.44	DA 10	0.593	1.41	2.77
9	C DA10	0.071	1.590	56.17	C DA10	0.589	1.50	3.44
10	DA 54	0.100	1.371	38.27	DA 54	0.515	2.67	15.57
11	DA 62	0.043	1.182	73.45	DA 62	0.512	2.15	16.07
12	Donor NP	0.162	-	-	Donor	0.610	-	-
13	Acceptor NP	-	1.079	-				

^aaverage life time, ^benergy transfer efficiency.

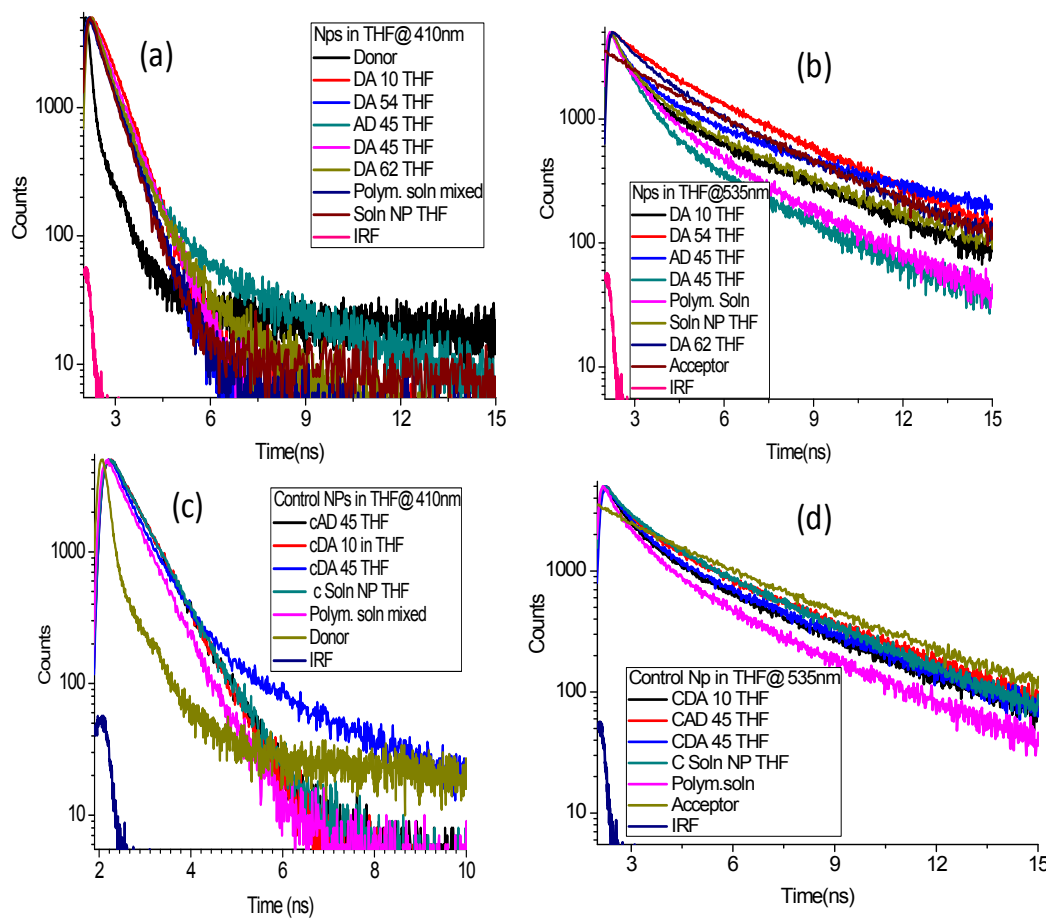


Fig. S11 Biexponentially fitted decay curves of bi-polymer nanoparticles in THF (a) Fluorescence life-time decay curves of catalysed NPs at 410 nm (b) At 535 nm (c) Fluorescence life-time decay curves of catalyst-free NPs at 410 nm. (d) At 535 nm

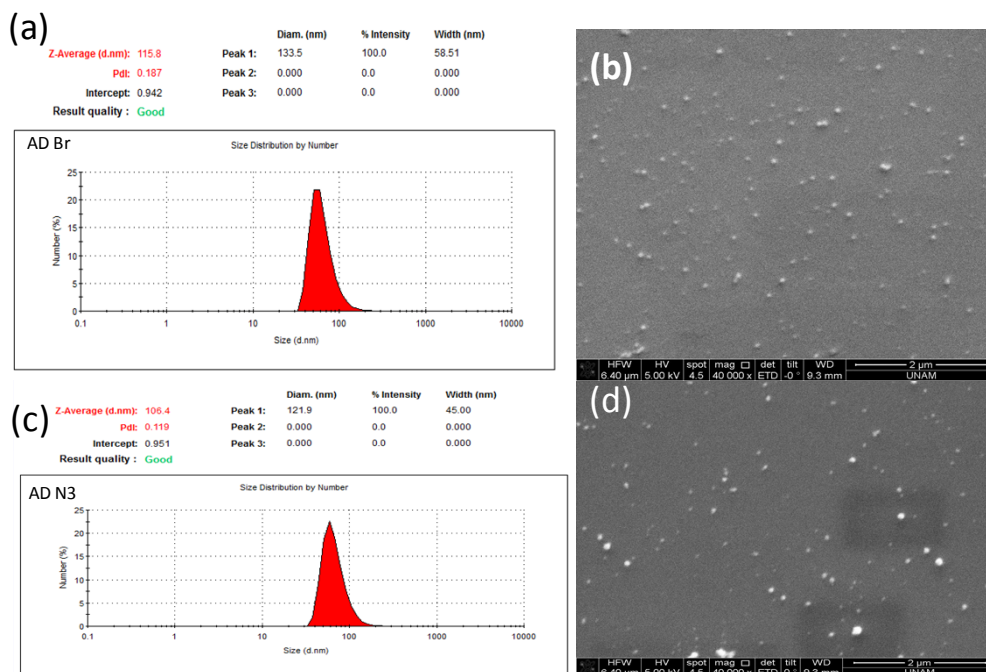


Fig. S12 (a) DLS: Zeta size of AD Br NP from non-functionalized polymers (115 nm) (b) SEM micrograph of AD Br (c) DLS: Zeta size of AD N3 formed by click reaction (106 nm) (d) SEM micrograph of AD N3.

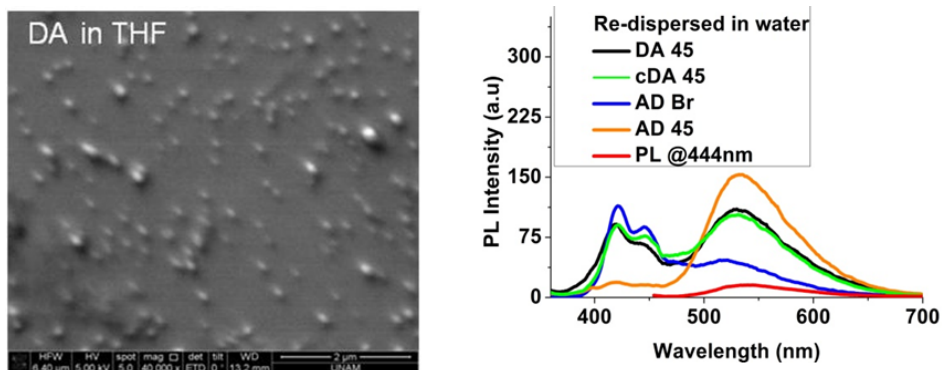


Fig. S13 SEM micrograph of bi-polymer NPs dispersed in THF and emission spectra of re-dispersed bipolymer NPs in water including ADBr (λ_{ex} =350 nm).

Table S3 Time resolved-fluorescence life time of tandem nanoparticles in water (intensity weighted)

S/N	NPs in water	τ_{avr} [ns] @420nm	τ_{avr} [ns] @535nm	η [%]
1.	RAD	0.055	1.692	66
2.	T Sol	0.048	1.287	70
3.	T.NPs mixed	0.158	0.091	-
4.	DAR 12	0.101	1.908	38
5.	DAR 6	0.108	2.461	33
6.	DAR 4	0.126	2.282	22
7.	Donor NP	0.162	-	

^aaverage life time, ^benergy transfer efficiency.

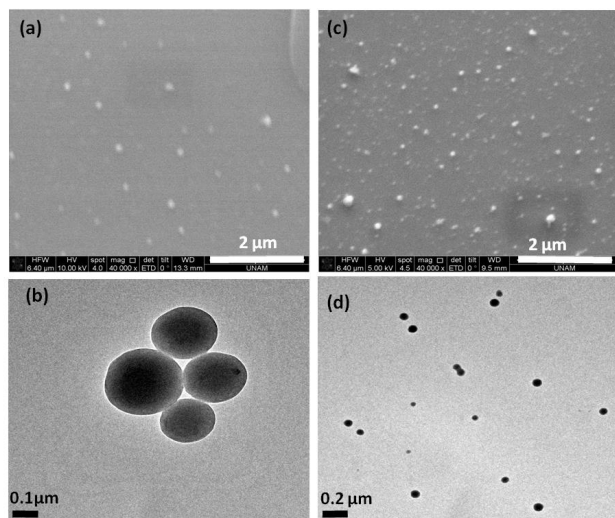


Fig. S14 (a) SEM micrograph of DAR 12% (b) TEM micrograph of DAR 12% (c) SEM micrograph of DAR 6% (d) TEM micrograph of DAR 6%

Z-Average (d.nm): 101.4	Peak 1: 66.33	100.0	21.02
Pd: 0.129	Peak 2: 0.000	0.0	0.000
Intercept: 0.953	Peak 3: 0.000	0.0	0.000

Result quality : Good

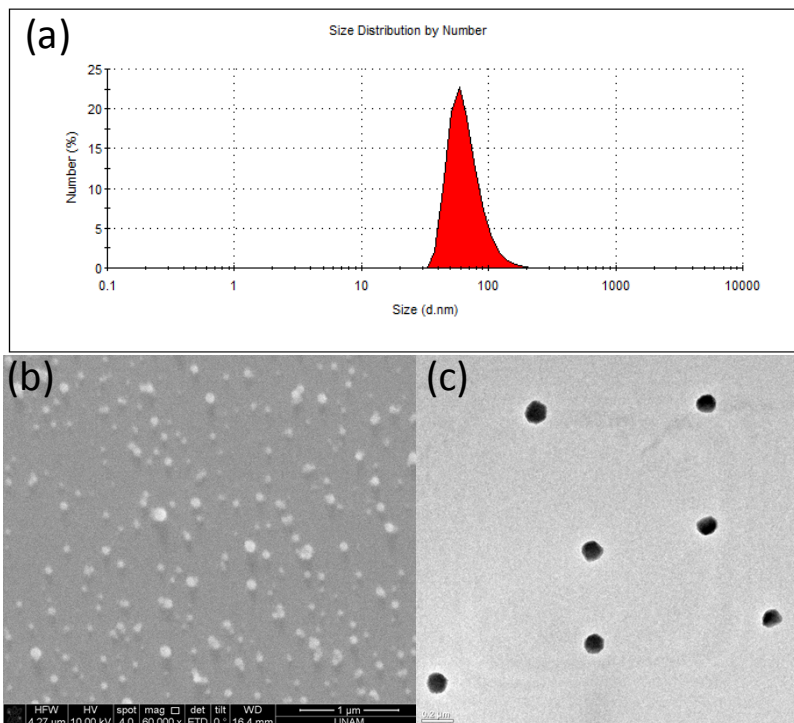


Fig. S15 Size and morphology of DAR 4% NPs (a) DLS (b) SEM and (c) TEM image

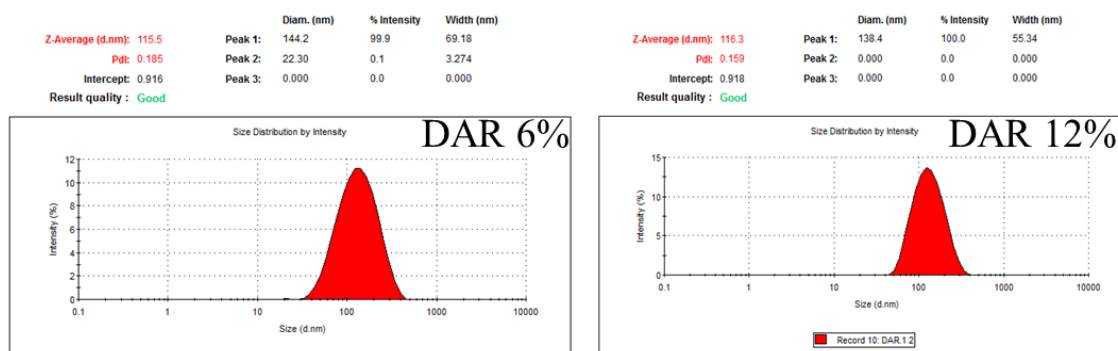


Fig. S16 DLS histograms of DAR 6% NPs of DAR 12% NPs.

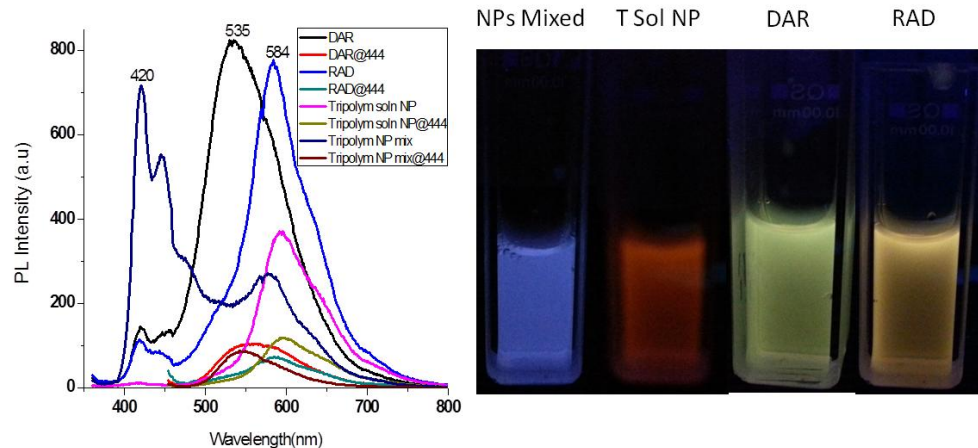


Fig. S17 The emission spectra of tandem NPs with their corresponding emission colors. ($\lambda_{ex}=350$ nm)

Table S4: x-y Colour coordinates at varying currents.

Current (mA)	20	30	40	50	60
x	0.3502	0.3511	0.3506	0.3496	0.3504
y	0.3846	0.33857	0.3879	0.3852	0.3878

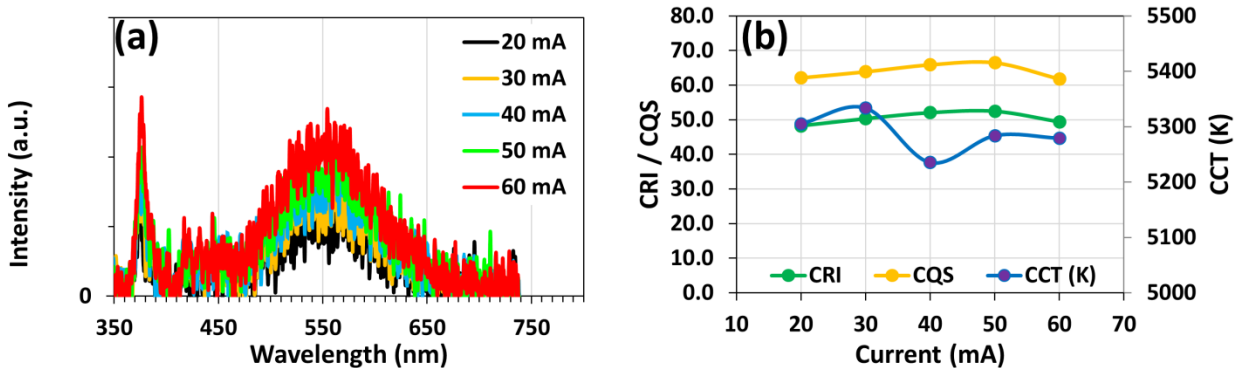


Fig. S18 (a) The spectra and (b) CRI, CQS, and CCT of the DAR 4% catalyst tandem nanoparticle integrated white LED at varying current levels.

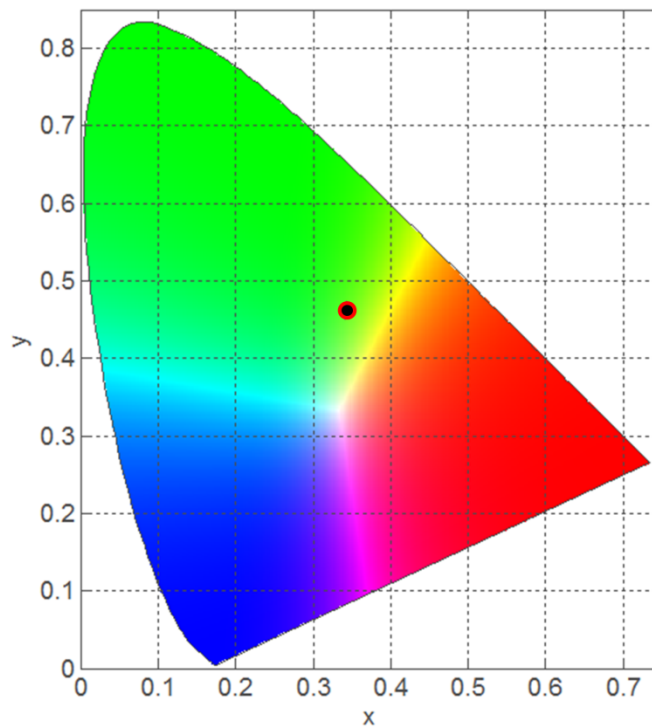


Fig. S19 The chromaticity point of the DAR 4% catalyst tandem nanoparticle integrated LED on CIE 1931 chromaticity coordinate.

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