White-Emitting Conjugated Polymer/Inorganic Hybrid Spheres: Phenylethynyl and 2,6-Bis(pyrazolyl)pyridine Copolymer Coordinated to Eu(tta)$_3$

*Yemineni S. L. V. Narayana, Supratim Basak, Martin Baumgarten, Klaus Müllen, and Rajadurai Chandrasekar**

The synthesis of two cyan color (blue and green emission) displaying high molecular weight 2,6-bis(pyrazolyl)pyridine-*co*-octylated phenylethynyl conjugated polymers (CPs) is presented. The conjugated polymers are solution-processed to prepare spin coated thin films and self-assembled nano/microscale spheres, exhibiting cyan color under UV. Additionally, the metal coordinating ability of the 2,6-bis(pyrazolyl)pyridine available on the surface of the CP films and spheres is exploited to prepare red emitting Eu(III) metal ion containing conjugated polymer (MCCP) layer. The fabricated hybrid (CP/MCCP) films and spheres exhibit bright white-light under UV exposure. The Commission Internationale de l'Eclairage (CIE) coordinates are found to be ($x = 0.33$, $y = 0.37$) for hybrid films and ($x = 0.30$, $y = 0.35$) for hybrid spheres. These values are almost close to the designated CIE coordinates for ideal white-light color ($x = 0.33$, $y = 0.33$). This easy and efficient fabrication technique to generate white-color displaying films and nano/microspheres signify an important method in bottom-up nanotechnology of conjugated polymer based hybrid solid state assemblies.

1. Introduction

π-conjugated polymers[1–6] (CPs) play an important role in organic electronic devices[2a] such as polymer light emitting diodes (PLEDs),[2b] back light of liquid crystal displays, full color display applications, light emitting electrochemical cells (LEECs),[2c] solar cells,[2d] photonic crystals,[2e] photonic devices,[2f] and organic field effect transistors (OFET).[2g] Amongst CPs, particularly the design and synthesis of white light-emitting polymers have attracted much attention because of their direct applications in display and lighting devices.[2h] Additionally, CP-based spherical beads, spheres, and colloidal crystals are attractive in the area of photonic crystals and nonlinear optical studies.[2i–k] An ideal white light-emitting system requires to emit three primary BGR (blue, green, and red) or two BY (blue and yellow) colors, so that the emission spectrum covers the whole visible range wavelength from 400 to 700 nm.[2l,15a,16] A straightforward strategy to acquire solid state white emission is to integrate several light emitters with dissimilar but complementary emission wavelengths into a single polymer layer, in order to realize synergistic color emission. However, this method suffers from unwanted energy transfer from the high band gap chromophores to lower band gap moieties.[2m–o]

In this regard, metal containing conjugated polymers (MCCPs)[4–6] are of interest, since they offer a wide option for color tunability by varying the choice of photo luminescent transition metal (Ru^{3+}, Ir^{3+})[4a–d] and lanthanide (Ln^{3+})[5,6,18a] ions. In MCCPs, three types of construction approaches are followed: i) the metal can be tethered to the conjugated polymer back bone via alkyl linker chains carrying ligands;[7] ii) self-assembly of ditopic ligands[8,18d] with metal ions to form linear metallo-supramolecular polymers; and iii) direct coordination of luminescent metal ions to the conjugated polymeric ligand back bone.[5f,9] We adopted the synthetically challenging last approach, since this class of polymer offers the possibility to achieve a range of colors by the incorporating a variety of luminescent metal ions on the polymer film surface via spin- or dip-coating techniques.[5f,10,15b] Additionally, by following our original approach,[5f,18d,e] coordination chemistry on the surface of the self-assembly solids (e.g., spheres, particles, tubes, etc.) can be performed, to prepare CP/MCCP containing soft microspheres emitting wide spectrum of colors.

Hence, we have envisioned fabricating white-emitting CP/MCCP films and self-assembled nano/microscale CP/MCCP hybrid spheres. Generally, in solid state, most of the blue emitting conjugated homo and copolymers also show green emission due to aggregation induced excimer formation.[11,13] In order to benefit from these mixed blue/green (cyan) dual emissions, we intended to copolymerize of 2,6-bis(pyrazolyl)pyridine (BPP) ligand with octylated phenylethynyl (PhE) derivatives to prepare a cyan color exhibiting conjugated copolymer films and

Y. S. L. V. Narayana, S. Basak, Prof. R. Chandrasekar
Functional Molecular Nano-/Micro-Solids Laboratory
School of Chemistry
University of Hyderabad
Prof. C. R. Rao Road, Hyderabad–500046, India
E-mail: chandrasekar100@yahoo.com
Prof. Dr. M. Baumgarten, Prof. Dr. K. Müllen
Max Planck Institute for Polymer Research
Ackermannweg 10, D-55218, Mainz, Germany

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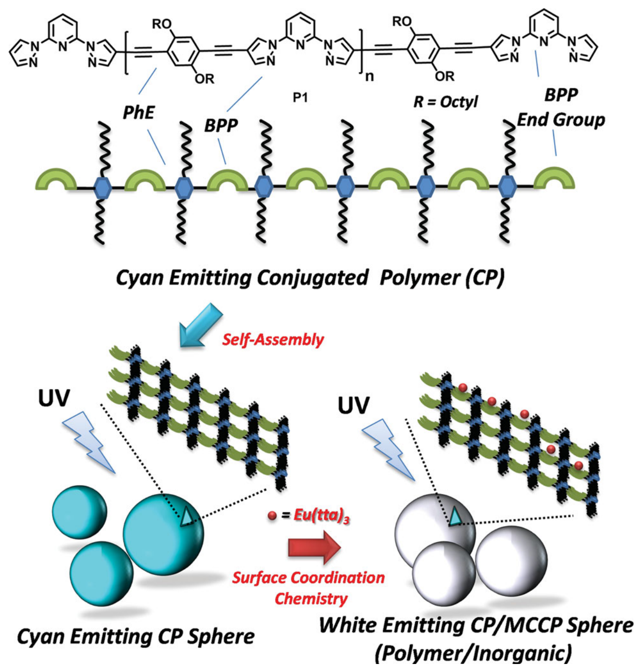


Scheme 1. Illustration of white emitting nano/microspheres obtained from Eu(III) coordinated conjugated copolymer **P1** via self-assembly. BPP: 2,6-bis(pyrazolyl)pyridine CP: conjugated polymer, PhE: octylated phenylethynyl, MCCP: metal containing conjugated polymer.

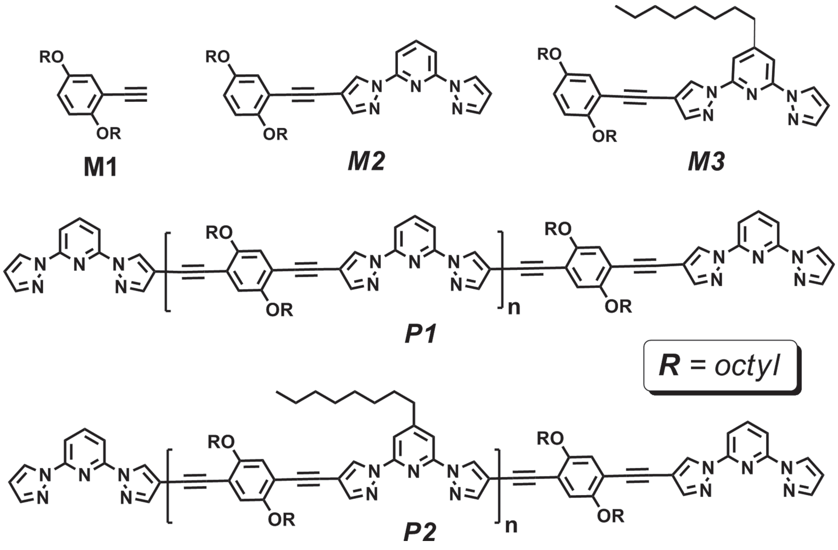
nano/micro solid structures as reactive CP template for metal coordination on BPP sites. Finally, by incorporating red phosphor Eu(III) ions on the surface of these copolymer templates, we envisioned achieving CIE coordinates close to white color ($x = 0.33$, $y = 0.33$).

In this paper, we report our novel one-pot approach to accomplish white color emitting CP/MCCP hybrid films and nano/microspheres (**Scheme 1**). At first, we present the syntheses of model compounds (**M1–M3**) and copolymers **P1** and **P2** (**Scheme 2** and Scheme S1, Supporting Information), and the self-assembly of **P1** to form cyan emitting copolymer films and spheres. Preparation of white-color emitting films/spheres via coordination with Eu(III) will also be discussed. Additionally, the photo physical and energy transfer properties of model **M3** Eu(tta)$_3$ complex were compared with Eu(tta)$_3$ coordinated bulk polymers of **P1** and **P2** (Figures S10–S15, Suppporting Information). Meticulous examinations of self-assembled white emitting spheres using electron microscopy (FESEM/SEM/TEM), atomic force microscopy (AFM), confocal μ-Raman spectroscopy (CRS), and confocal fluorescence microscopy (CFM) techniques will also be reported.

2. Result and Discussion

2.1. Syntheses

For the synthesis of cyan emitting copolymer **P1**, 1,4-diethynyl-2,5-bis(octyloxy)benzene (DEB) **3** was prepared from hydroquinone.[12a] 2,6-bis(4-iodo-1H-pyrazol-1-yl)pyridine (BPP) **1** was synthesized from 2,6-dibromopyridine in yields >80%.[12b] Formation of cyan emitting copolymer **P1** end capped with BPP was carried out under Sonogashira cross coupling reaction conditions using BPP and **3** in presence of diisopropyl amine/THF (see Supporting Information).[12c] The organic layer obtained during workup was redissolved in CHCl$_3$, followed by precipitation using MeOH to isolate off-brown color precipitate of **P1**. Further, the polymer was purified by washing with boiling MeOH, acetone, and at room temperature hexanes and MeOH solvents followed by cold CHCl$_3$ to isolate a yellow powder of **P1** (M_n = 5.5 KDa by ^{1}H NMR, GPC data: M_n = 5.6 KDa, M_w = 18.7 KDa, PDI = 3.34). For the synthesis of highly soluble copolymer **P2**, a similar procedure was adopted using octylated-BPP **2** and **3** to get a yellow powder with a higher molecular weight (M_n = 10.6 KDa by ^{1}H NMR, GPC data: M_n = 8.1 KDa, M_w = 62.5 KDa, PDI = 7.68).



Scheme 2. Chemical structures of model compounds (**M1–M3**) and copolymers (**P1–P2**), R = Octyl chain.

2.2. White Emitting Polymer Films

The optical absorption and emission spectra of polymers (**P1** and **P2**) in solution and spin coated films are presented in **Figure 1** and Supporting Information, Figure S1a,b, and Table S1. In solution state, **P1** and **P2** show mostly bluish cyan color (Figure S9, Supporting Information) with emission peaks maxima at 401, 440, 460 nm, and 399, 439, 466 nm, respectively for the excitation (λ_{ex}) performed at 370 nm. The spin coated (from CHCl$_3$) dry thin films of **P1** and **P2** show green emission (400–650 nm range) due to aggregation induced excimer-like behavior.[11,13] A solid solution of **P1** prepared with a non-emissive polymer matrix (poly((tetrahydrofuran)-tetrathane-2900))

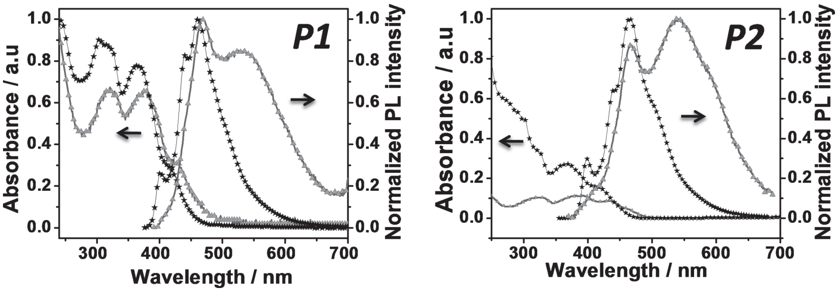


Figure 1. Optical absorption spectra of polymers **P1** and **P2** in $CHCl_3$ (⋆), and spin casted film (△). PL spectra of polymers in $CHCl_3$ solution (⋆), and spin-casted film (△).

supported this aggregation phenomenon. Upon increase of terathane/**P1** ratio the solid film showed decrease in green emission due to the segregation of polymer chains. At 1:1 ratio (terathane/**P1**) the solid film almost behaved like solution (Figure S2, Supporting Information). The polymer film emission intensity of $I_{\text{blue}}/I_{\text{green}}$ was adjusted by tuning the polymer film thickness[5f,14] in such a way that a cyan color light was obtained. We found that spin coating of a $CHCl_3$ solution of concentration of 12.37 mg mL^{-1} of **P1** emitted a good cyan color with $I_{\text{blue}}/I_{\text{green}} \approx 1$ (Figure S3, Supporting Information). Furthermore, by using the metal coordination ability of main chain BPP tridentate ligand units of polymers **P1** and **P2**, incorporation of red emitting $Eu^{(III)}(tta)_3$ (tta = thenoyltrifluoroacetonate) was envisioned to achieve a final white-color light.[5f] For this the **P1** film was dipped in a 20 mL methanol solution containing 0.5 mg $Eu(tta)_3$ complex for half an hour. Here, the amount of $Eu(tta)_3$ complex formation was adjusted to control the intensity of the $Eu^{(III)}$ centered red phosphorescence [$^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions] according to the intensity of $I_{\text{blue}}/I_{\text{green}}$ emissions to attain good quality white color. UV light exposure of **P1** film reacted with $Eu(tta)_3$ complex showed a white-color light due to the mixing of 474/541/613 nm emissions (**Figure 2**a and Figure S1c, Supporting Information). Similarly, for **P2**, white light (Figure 2b and Figure S1d, Supporting Information) was obtained by controlling the polymer film thickness (c = 16.87 mg mL^{-1} of $CHCl_3$) and $Eu(tta)_3$ concentration (Figure S4, Supporting Information).

The purity of the emitted white light was analyzed by chromaticity diagram (Figure 2c and Figure S1e, Supporting Information), for which the CIE (x and y) coordinates were found to be (0.33, 0.37) and (0.33, 0.37) for films made from **P1** and **P2**, respectively, which are nearly close to the designed coordinates for perfect white light (0.33, 0.33). Moreover, the contribution of energy transfer process between the polymer backbone and Eu^{III} coordinated centre in the white emitting polymer **P1** was investigated (Figure S15, Supporting Information). Excitation of white-light emitting $Eu(tta)_3$ coordinated **P1** polymer at 373 nm (corresponding to the absorption maximum of **P1**), showed all luminescence bands of pure polymers and $Eu^{III}(tta)_3$ (Figure S15c, Supporting Information). While direct excitation of the same polymer at 413 nm (corresponding to the absorption of $Eu(tta)_3$) exhibited no emission from $Eu^{III}(tta)_3$ (Figure S15c, Supporting Information), at this wavelength, pure $Eu(tta)_3 \cdot 3H_2O$ showed red emission (Figure S15d, Supporting Information). Similar behavior was observed for the $M_3 \cdot Eu(tta)_3$ model complex (Figure S14, Supporting Information). This observation established the reaction of six coordinated $Eu(tta)_3$ molecules with BPP unit of the copolymer and the formation of nine coordinated $[PE\text{-}(BPP(Eu(tta)_3))]_n$ complexes[18b] on the polymer surface. Moreover, the excitation spectrum of white-light emitting $Eu(tta)\text{-}_3$ coordinated **P1** polymer film monitored at λ_{em} of 613 nm (J = 2 transition) showed two maxima at 373 and 431 nm, matching with the absorption of pure **P1** film and $Eu(tta)_3$ (Figure S15e, Supporting Information), thus suggesting the operating energy transfer process from the polymer **P1** backbone to the Eu(III) center.[5f,17,18c]

2.3. White Emitting Nano/Microscale Polymer Spheres

Since the reaction of $Eu(tta)_3$ on the cyan color films (**P1** and **P2**) was inhomogeneous, the resultant white color intensity varied along the film surface (Figure S1, Supporting Information). Hence, a self-assembly route was adopted to prepare CP/MCCP hybrid spheres. In a representative procedure, 1 mg of **P1** dissolved in 1 mL of tetrahydrofuran (THF). The solution was kept for 15 min undisturbed to stabilize growth of spheres. Illumination of the THF solution containing spheres with laser light displayed a fine Tyndall effect indicating the formation of solution-stable nanostructures (Figure S8, Supporting Information). Further more dynamic light scattering (DLS) experiment (**P1** in THF) confirmed the presence of nanospheres in the solution with the hydrodynamic radius in the range of r_H = 118–143 nm. Two drops of this polymer solution were drop

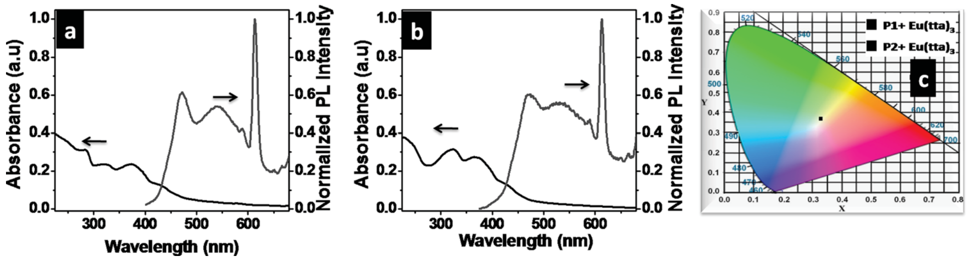


Figure 2. a,b) Optical absorption and emission spectra of white emitting $Eu(tta)_3$ coated **P1** and **P2** CP films. c) Emission color of $Eu(tta)_3$ coated **P1** and **P2** film in a CIE 1931 2° Standard Observer chromaticity diagram.

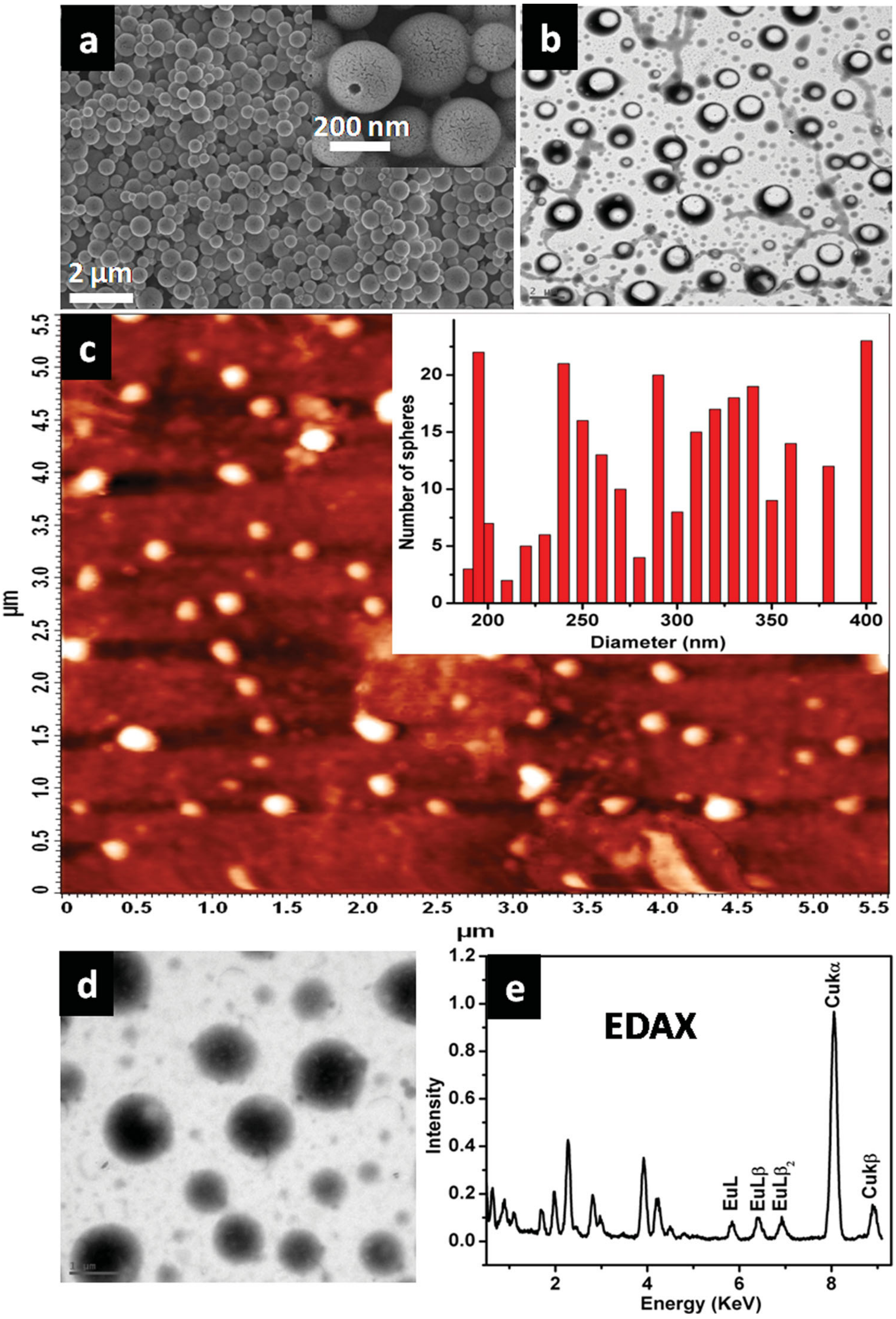


Figure 3. a) FESEM images of CP spheres obtained from **P1** (scale bar is 2 µm), (inset shows a closer view of the spheres; b) bright field TEM image of spheres (scale bar is 2 µm); c) AFM image of nanoscale spheres; (inset plot estimates the diameter/number of spheres in an area shown in (c); d) TEM image of Eu(III) coordinated CP spheres (hybrid CP/MCCP) (scale bar is 1 µm). e) EDAX spectrum exhibiting Eu(III) ions peaks.

casted on a clean glass substrate at room temperature for field-emission SEM, AFM, and confocal fluorescence microscope studies or on a carbon coated grid for TEM analysis. The electron microscopy (FESEM and TEM) and AFM examination of the sample revealed the formation of nano and microspheres (**Figure 3**a–c). TEM images of CP spheres displayed a relatively weak contrast as usually observed for soft organic structures (Figure 3b). AFM cross-section analysis of several spheres showed that the diameter is in the range of ≈190–400 nm (Figure 3c). The self-assembly of cyan emitting CP into spheres is possibly mediated by the π–π stacking interactions of the polymer aromatic units, thereby increasing the close packing of

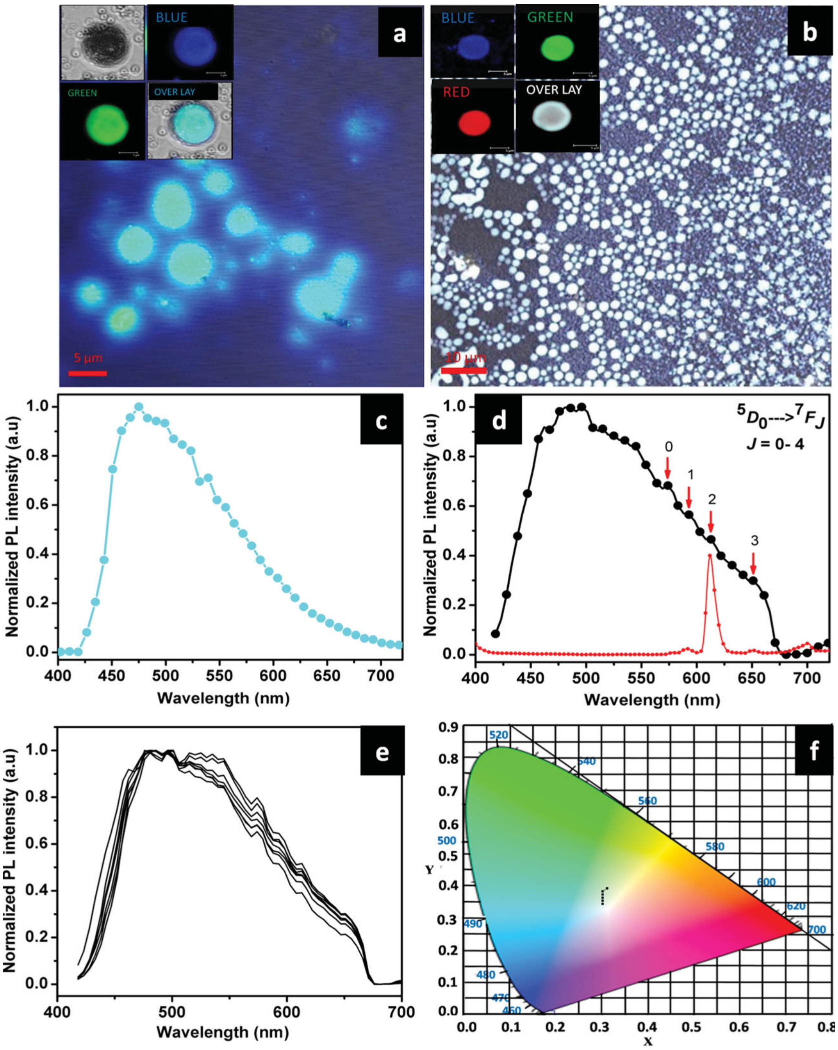


Figure 4. Confocal fluorescence images of CP and hybrid CP/MCCP spheres. a) Cyan emitting CP spheres (insets show the bright field image of a single sphere obtained from **P1**, displaying mixed cyan emission due to blue and green dual emissions. (scale bar is 5 µm). b) White emission of hybrid CP/MCCP spheres (insets show blue, green and red emissions from CP/MCCP spheres, and the resultant white color) (scale bar is 10 µm). c,d,e) Confocal microscopy fluorescence spectra of cyan emitting CP sphere obtained from **P1**, white emitting hybrid CP/MCCP sphere, and six CP/MCCP spheres of varying sizes, respectively. f) CIE 1931 2° Standard Observer chromaticity diagram of white emission color displayed by six MCCP spheres ($x = 0.30$ for 6 spheres and $y = 0.35, 0.36, 0.37, 0.38, 0.39, 0.40$), corresponding to their spectra shown in (e) ($\lambda_{ex} = 365$ nm).

the hydrophobic octyl-chains forming a sphere like structures (Scheme 1). In order to obtain white color from cyan emitting spheres, our earlier original approach (i.e., coordination chemistry on the surface of self-assembled solids) was followed.[18d,e] Firstly, the CP spheres templates were grown in THF solution of **P1**, as mentioned before. Secondly, by injecting a THF solution of $Eu(tta)_3 (H_2O)_3$ (0.869 mg/0.02 mL) to the solution containing the CP spheres, followed by gentle shaking, a layer of $[(Eu(tta)_3)(\textbf{P1})]$ coordination complex[18d,e] was formed on the surface of the spheres. The possible mechanisms of $[(Eu(tta)_3)(\textbf{P1})]$ complex formation on the spheres are: i) by the coordination of $Eu(tta)_3$ with the surface exposed BPP units and ii) diffusion of $Eu(tta)_3$ into the pores or defective sites of spheres, and then coordinating with BPP units thereby blocking the pores and defects. Examination of the TEM-bright field images obtained from the CP/MCCP spheres exhibited an apparent dark contrast for the areas coated with Eu(III) complex compared to light contrast displayed by the unreacted CP spheres (Figure 3b,d). In addition, the energy dispersive X-ray spectroscopy analysis (EDAX) performed on the surface of a sphere clearly confirmed the presence of Eu ions (Figure 3e).

In order to confirm the appearance of cyan and white colors from both CP and CP/MCCP spheres, respectively, a scanning confocal fluorescence microscopy measurement was performed (**Figure 4**a–f). The topographic structural data were directly coupled with the spectroscopic properties of the specimen. For excitation Ar^+ (UV-365) laser was used. As expected the **P1** based CP spheres displayed a cyan color due to the mixing of blue and green emissions. Whereas CP coated with Eu(III) complex (CP/MCCP spheres) showed emission spectrum covering the whole visible region (400–700 nm), as a result exhibiting a remarkable white light. By using confocal data, the obtained CIE (x, y) purity of the emitted white-light of six various sized spheres provided the same x value = 0.30 and slightly varied y values = 0.35, 0.36, 0.37, 0.38, 0.39, 0.40, which are nearly close to the designated coordinates for ideal white-light ($x = 0.33$, $y = 0.33$) (Figure 4f).

3. Conclusions

We have demonstrated for the first time an efficient technique for the preparation of white emitting CP/MCCP hybrid films and nano/microscale spheres by employing self-assembly techniques, that is, formation of film/spheres template from a novel cyan color emitting copolymer **P1** in THF and subsequent reaction of $Eu(tta)_3$ with **P1** selectively, on the surface of the film/spheres. The self-assembled hybrid structures displayed brilliant white-light under UV. This simple and efficient fabrication method to generate white-color displaying films and nano/microspheres is an important method in the bottom-up nanotechnology of conjugated polymer based hybrid solid state assemblies. This general principle can be applied to get wide variety of luminescent structures displaying diverse colors.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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