Emission Enhancement via Formation of ‘Controlled’ Aggregations in the Hybrid Chromophoric Surfactant Amphiphile/Silica Self-assembled Nanocomposites **

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Scheme-S1

1. i) n-BuLi, THF (dry), -78°C
   ii) Tri-isopropyl borate

2. Reaction with K$_2$CO$_3$, DMF, 60°C

3. Product after Pd(PPh$_3$)$_4$, 1,2-Dimethoxyethane, 2M Na$_2$CO$_3$, Reflux for 1 day
Scheme-S2

TBACl, NaOH, THF, H₂O → Br-(CH₂)₁₁-OH, 70°C

90°C → Pd(OAc)₂, Et₃N, (o-tolyl)₃P

(4) → (5)
Experimental Section

$^1$H NMR spectra were recorded (Unity-300 spectrometer at 300 MHz) in CDCl$_3$ solutions. Images of spin-coated or deep-coated nanocomposites mounted on carbon tape were acquired on a field-emission scanning electron microscope (JSM-6500 F, JEOL); to enhance the conductivity of the specimen, a layer of platinum was sputtered (duration 30 s, current 30 mA, pressure 4 Pa). TEM micrographs were observed under JEOL, JEM-2010. UV-Vis absorption spectra were measured with HP8453 diode array spectrometer. Photoluminescence spectra were obtained on a SpectraPro-150 with Muller SVX 1450 xenon lamp and external quantum efficiencies ($F$) were measured using an integrating sphere method. X-ray diffraction measurements for nanocomposites films were done with a diffractometer (Bede D1 type) with Cu$_{K\alpha}$ radiation.

Synthesis of Terphenyl chromophore amphiphile (PPP-C11):

4-Biphenylboronic acid (1): To a cooled solution (-78°C) of 4-bromobiphenyl (9.3 g, 40 mmol) in 100 mL dry THF, was added dropwise, 16 mL of a 2.5 M solution of $n$-BuLi in hexane. This mixture was stirred and kept at -78°C for 2.5 h. Color of the solution became green to pale white. A solution of tri-isopropyl borate (15.0 g, 80 mol) was slowly added over 30 minutes after which the reaction mixture was allowed to warm up to room temperature overnight. The resulting greenish yellow mixture was acidified with 60 mL of a 10% HCl solution and stirred for 16 h at room temperature. The crude product was extracted into diethyl ether (3 x 100 mL), and washed successively with a concentrated sodium carbonate solution and water. The ether was removed by distillation and the crude product was recrystallized twice from a water/ethanol mixture (95/5). The crystals were dried under vacuum overnight at 60°C to obtain 6.0 g (76%) of off-white 4-biphenylboronic acid. $^1$H NMR (300 MHz, Acetone-$d_6$): d= 7.98 (d, 2H; ArH), 7.68 (t, 4H; ArH), 7.48 (t, 2H, ArH), 7.43 (d, 1H, ArH), 7.38 (s, 2H, -B(OH)$_2$).
I-Phenyl-C11 (2): *p*-Iodophenol (6.0 g, 29.7 mmols) and K$_2$CO$_3$ (5.1 g, 37.1 mmols) were mixed in dimethylformamide (DMF) and stirred for 30 min. Resulting solution turned reddish. To it was added 11-Bromo-1-undecanol (7.45 g, 29.7 mmol) and the reaction mixture was stirred and heated at 60°C for one day. Milky white solution thus obtained was acidified by dilute HCl and then extracted with CH$_2$Cl$_2$/water. The organic layer was washed with saturated NaCl solution, dried over MgSO$_4$. Dichloromethane was evaporated in vacuo and solid obtained was recrystallized from ethyl acetate to give white product (82%). $^1$H NMR (300 MHz, CDCl$_3$) δ= 7.52 (d, 2H; ArH), 6.65 (d, 2H; ArH), 3.88 (t, 2H; -OCH$_2$), 3.61 (t, 2H; -CH$_2$), 1.73 (m, 2H; -CH$_2$), 1.54 (m, 2H; -CH$_2$), 1.51-1.27 ppm (m, 14H; -CH$_2$).

Terphenyl chromophore amphiphile (PPP-C11) (3): 1 (0.5 g, 2.6 mmols) and 2 (1 g, 2.5 mmols) were mixed in dimethoxyethane (DME) and stirred in round bottom flask under nitrogen atmosphere. After about 10 min, when the mixture turned brownish, 2M Na$_2$CO$_3$ (0.57 g, 5.37 mmol) solution in water was added. After a few minutes, solution turned black. It was heated at 85°C under nitrogen for two days. The mixture was then acidified with dilute HCl and extracted with dichloromethane and water. Organic layer was washed with saturated NaCl and dried over MgSO$_4$ and the solvent was evaporated in vacuo. After double recrystallization of the crude from chloroform, a pale white product 3 was obtained (Yield= 62%). $^1$H NMR (300 MHz, CDCl$_3$) δ= 7.70 (d, 2H; ArH), 7.65 (t, 3H; ArH), 7.45 (m, 4H; ArH), 7.43 (m, 2H; ArH), 6.98 (d, 2H; ArH), 3.98 (t, 2H; -OCH$_2$), 3.62 (t, 2H; -CH$_2$-OH), 1.77 (m, 2H; -CH$_2$), 1.53-1.29 ppm (m, 14H; -CH$_2$), EI-MS (32, 41, 55, 246, 306, 416).

**Synthesis of Fluorene-Stilbene chromophore amphiphile (FL-Stilbene-(C11)$_2$):**

FL-(C11)$_2$ (4): Tetrabutylammonium chloride (TBACl) (0.08 g, 12.34 mmol) was added in 50 wt% NaOH in water and heated at 70°C. 11-Bromo-1-undecanol (3.1 g, 12.34 mmol) was added to it after some time. Then 2, 7-dibromofluorene (2 g, 6.17 mmol) in THF was slowly added to the
mixture, stirred and heated at 70°C for two days. After cooling the reaction mixture to room temperature, THF was removed on rotar. The mixture was poured into water and acidified with dilute HCl and then extracted with ethyl acetate. Organic phase was washed with saturated NaCl, dried over MgSO$_4$ and after removing EA on rotar, crude was obtained. The product was purified by column chromatography (SiO$_2$, 20% EA/Hexane) to give 2.5 g (60.8%) highly viscous oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.47 (d, 2H; ArH), 7.42 (d, 4H; ArH), 3.57 (t, 4H; -CH$_2$OH), 1.87 (m, 4H; -CH$_2$), 1.50 (m, 4H; -CH$_2$), 1.23-0.97 ppm (m, 32H; -CH$_2$).

FL-Stilbene-(C11)$_2$ (5): Compound 4 (1 g, 0.9 mmol), styrene (0.24 g, 2.4 mmol), palladium (II) acetate (0.004 g, 0.02 mmol), tri-orthotoluene phosphine (0.01 g, 0.04 mmol) and triethylamine (0.57 g, 7.7 mmol) were heated at 90°C for one day in a hard glass tube sealed under nitrogen. The reaction mixture was allowed to cool to room temperature and after evaporating triethyl amine on rotar, was extracted with dichloromethane, water and saturated NaCl. Organic phase was dried over MgSO$_4$ and the solvent was evaporated in vacuo. The product (Yield= 67%) was obtained by column chromatography (SiO$_2$, 3:7 EA/Hexane). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.63 (d, 2H; ), 7.54 (m, 6H, ArH), 7.38 (m, 4H; ArH), 7.27 (d, 4H; ArH), 7.17 (d, 4H; =CH), 3.55 (t, 4H; -CH$_2$OH), 1.99 (m, 4H; -CH$_2$), 1.46 (t, 4H; -CH$_2$), 1.23-1.03 ppm (m, 32H; -CH$_2$). MS (366, 369, 395, 540, 711).

Chromophore amphiphile/silica hybrid nanocomposites formation by evaporation-induced self-assembly (EISA): Precursor solutions were synthesized from tetraethyl orthosilicate (TEOS, Si(OC$_2$H$_5$)$_4$), chromophoric amphiphiles (PPP-C11 and FL-Stilbene-(C11)$_2$), and HCl catalyst prepared in ethanol/water solvent. The final reactant mole ratio for nanocomposites prepared from PPP-C11 and FL-Stilbene-C11, were 1 TEOS:30 ethanol:5 H$_2$O: 0.1 HCl: 1 PPP-C11 and 1 TEOS:30 ethanol:5 H$_2$O: 0.1 HCl: 0.5 FL-Stilbene-(C11)$_2$, respectively. In a typical preparation,
TEOS, ethanol, water and dilute HCl were stirred and heated at 35°C for half an hour. To this solution was added the chromophoric surfactant in ethanol and stirred for three hours. Films were prepared on quartz by evaporative spin-coating (1,500 r.p.m.), or dip-coating (at a rate of 30 cm min⁻¹). During deposition, preferential evaporation of THF concentrates the depositing film in water and nonvolatile silica and chromophoric surfactant. The progressively increasing surfactant concentration drives self-assembly of chromophore amphiphile/silica micelles and their further organization into ordered liquid crystalline mesophases.