Supporting Information

Molecular-oriented self-assembly of small organic molecules into uniform microspheres

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Experimental details

1. Materials

The organic compounds of 4-(bis(4-methoxyphenyl)amino)benzaldehyde 4-(diphenylamino)benzaldehyde, and 1-(4-fluoro-2-hydroxyphenyl)ethan-1-one, were purchased from Sigma-Aldrich and were used without further treatment. Ethanol (C₂H₅OH, HPLC grade), dichloromethane (DCM, HPLC grade), and KOH were purchased from Beijing Chemical Agent Ltd., China.

2. Synthetic procedure of DFHP and DFPHP

DFHP:

In a 500 mL round-bottomed flask, a mixture of 1-(4-fluoro-2-hydroxyphenyl)ethan-1-one (0.95 g) and KOH (0.51 g) was dissolved in the C₂H₅OH (200 ml), and stirred for 1h under room temperature. Then 4-(diphenylamino)benzaldehyde (1.69 g) in C₂H₅OH (30 ml) was then added dropwise. The temperature was just kept at room temperature for a further 48 h. The mixture was then added dropwise to water and extracted with CH₂Cl₂. The organic layer was separated out, dried over MgSO₄. And the residue solvents of CH₂Cl₂ were distilled in vacuo at 25 °C. By further recrystallization from acetonitrile/hexane solvents ($V_{acetonitrile} = 10$ ml, and $V_{hexane} = 5$ ml), the pure (*E*)-3-(4-(dipheylamino)-1-(4-fluoro-2-hydroxyphenyl)prop-2-en-1-one (DFHP) powder were obtained (1.96 g, 78 %). ¹H NMR (400 MHz, CDCl₃) δ 13.43 (s, 1H), 7.90 (dd, J = 15.5, 10.1 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 15.3 Hz, 1H), 7.32 (t, J = 7.7 Hz, 4H), 7.14 (dd, J = 14.6, 7.5 Hz, 6H), 7.03 (d, J = 8.5 Hz, 2H), 6.75–6.58 (m, 2H). ¹³C NMR (CDCl₃, 150MHz, ppm) δ : 193.25, 151.07, 145.41, 144.19, 137.44, 135.66, 134.43, 130.41, 130.30,

130.14, 127.57, 126.88, 126.03, 126.01, 125.81, 124.67, 124.20, 120.29, 118.21, 117.02, 113.86, 21.14. For [M+H]⁺: 410.16. Found: 410.22. Elemental Anal.: C, 76.20; H, 4.92; F, 4.64; N, 3.42; O, 7.82.

DFPHP:

(*E*)-3-(4-(bis(4-methoxyphenyl)amino)phenyl)-1-(4-fluoro-2-hydroxyphenyl)prop-2-en-1-o ne (DFPHP) (2.03 g, 70 %) was synthesized by changing the 4-(diphenylamino)benzaldehyde into 4-(bis(4-methoxyphenyl)amino)benzaldehyde(2.07 g) under the same reactive conditions above. ¹H NMR (400 MHz, CDCl₃) δ 13.50 (s, 1H), 7.89 (dd, *J* = 15.2, 11.3 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 15.2 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 4H), 6.92–6.82 (m, 6H), 6.72–6.59 (m, 2H), 3.82 (s, 6H). ¹³C NMR (CDCl₃, 150MHz, ppm) δ: 192.31, 167.94, 166.25, 166.09, 165.99, 156.89, 151.54, 145.97, 145.66, 139.34, 131.64, 131.56, 130.42, 130.23, 127.79, 127.59, 127.38, 127.29, 125.39, 118.25, 117.29, 115.51, 115.10, 114.92, 114.60, 106.87, 106.72, 105.07, 104.91, 77.23, 77.02, 76.80, 55.47, 29.68. For [M+H]⁺: 470.18. Found: 469.02. Elemental Anal.: C, 74.19; H, 5.15; F, 4.05; N, 2.98; O, 13.63.

3. Structural and optical characterizations of organic microstructures

The morphology and size of organic microstructures were also examined by field emission scanning electron microscopy (S-4800, Hitachi), and atomic force microscopy (AFM, Santa Barbara, CA) by dropping on a silicon wafer. The X-ray diffraction (XRD) patterns were measured by a D/max 2400 X-ray diffractometer with Cu K α radiation ($\lambda = 1.54050$ Å) operated in the 2 θ range from 5° to 30°, by using the samples on the silicon wafer.

Fluorescence images were recorded using an Olympus research inverted system microscope (FV1000-IX81, Tokyo, Japan) equipped with a charge couple device (CCD, Olympus DP71, Tokyo, Japan) camera. The excitation source is a mercury lamp equipped with a band-pass filter (330-380 nm for UV-light). The samples were prepared by placing a drop of solution onto a cleaned quartz plate, and then evaporated at room temperature.



Figure S1. ¹H NMR spectrum of DFHP recorded in CDCl₃ (400 MHz).



Figure S2. ¹H NMR spectrum of DFPHP recorded in CDCl₃ (400 MHz).



Figure S3. ¹³C NMR spectrum of DFHP recorded in CDCl₃ (150 MHz).



Figure S4. ¹³C NMR spectrum of DFPHP recorded in CDCl₃ (150 MHz).



Figure S5. FT-IR spectra of the DFHP (black line) and DFPHP (red line) solid form.



Figure S5. (a) TEM image of these as-prepared micro-scale hemispheres with a scale bar of 1.0 µm and DFPHP (red line). (b) The AFM image of these as-prepared micro-scale hemispheres.



Figure S6. (a) Absorption (dashed lines) and photoluminescence (solid lines) spectra of DFHP in *n*-hexane (black lines), toluene (blue lines), and DCM (red lines). And the PL spectrum of DFHP solid powder (pink line). Inset: the photographs of the DFHP powder under the excitation with the UV band (330-380 nm) from a mercury lamp. (b, c) The HOMO and the LUMO of the DFHP molecule simulated with DFT calculation at B3LYP/6-311G level. (d) Absorption (dashed lines) and photoluminescence (solid lines) spectra of DFHP in *n*-hexane (black lines), toluene (blue lines), and DCM (red lines). And the PL spectrum of DFHP solid powder (pink line). Inset: the photographs of the DFPHP powder under the excitation with the UV band (330-380 nm) from a mercury lamp. (e, f) The HOMO and the LUMO of the DFPHP molecule simulated with DFT calculation at B3LYP/6-311G level.

Figure S6 show the absorption (dashed lines) and photoluminescence (PL, solid lines) spectra of DFHP (Figure S6a) and DFPHP (Figure S6d) in CH₂Cl₂ (red), toluene (blue), and

n-hexane (black) solution, and their absorption peaks from 441-425 nm and 454-439 nm for these two organic compounds are consistent with the triphenylamine-centered π - π * transition. In low polar solvents such as *n*-hexane, both compounds of DFHP and DFPHP display the pronounced dual emission bands the emission peaks at 489 and 525 nm respectively, which can be assigned to the localized excited (LE) state; and the emissions at longer wavelengths around 550-610 nm originate from the donor-acceptor charge-transfer transition in these two organic molecules.

These two compounds of DFHP and DFPHP organic molecules show emission peaks at 504 and 611 nm in toluene solution, 603 nm and 678 nm in CH₂Cl₂, respectively. As is indicated, with increasing the high polar solvent (such as CH₂Cl₂), the remarkable red-shift emission bands of these two compounds are observed due to the strong charge transfer within these intra-molecular structures. In addition, the PL spectra of DHFP and DFPHP powders are dominated at 617 nm and 678 nm, respectively. In order to know the charge transfer characteristics of these two organic molecules, we perform the calculation of Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of the DHFP (Figure S6b and S6c) and DFPHP (Figure S6e and S6f) molecules by the DFT caculation at B3LYP/6-311G level. As indicated by the cauclation result, DHFP and DFPHP molecules both belong to the typical intramolecular charge-transfer (ICT) compounds, which is comfirmed by the obvious change of electric-cloud distribution between the HOMO and LUMO. Besides, DHPHP presents deeper red emission in CH₂Cl₂ solution on account of stronger HOMO/LUMO separation from the HOMO/LUMO of two molecules, which indicates wider optical band gap of DFPHP.

Name	DFHP
Empirical formula	$C_{27}H_{20}FNO_2$
Formula weight	409.15
Temperature	173.1500 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space Group	<i>P</i> -1
Cell Lengths (Å)	<i>a</i> 8.090(18) <i>b</i> 9.486(2) <i>c</i> 13.310(3)
Cell Angles (°)	α 92.34(10) β 96.68(9) γ 94.62(10)
Cell Volume (Å ³)	1009.94
Z: 2 Z': 0	Z : 2 Z' : 0

Table S1. Crystal data and structure refinement for DFHP (CCDC No. 1538294)

Name	DFPHP
Empirical formula	C ₂₉ H ₂₄ FNO ₄
Formula weight	469.17
Temperature	173.1500 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space Group	<i>P</i> 2 ₁ /n
Cell Lengths (Å)	<i>a</i> 10.479(7) <i>b</i> 11.511(5) <i>c</i> 12.942(5)
Cell Angles (°)	α 96.10(3) β 108.46(3) γ 116.47(3)
Cell Volume (Å ³)	1268.04.56
Z: 2 Z': 0	Z : 2 Z' : 0

 Table S2. Crystal data and structure refinement for DFPHP (CCDC No. 1539755)



Figure S7. The unit cell structure of DFHP crystals from different views along (a) a axis; (b) b axis; (c) c axis.



Figure S8. The unit cell structure of DFPHP crystals from different views along (a) a axis; (b) b axis; (c) c axis.



Figure S9. (a) The simulated equilibrium morphology of DFHP molecules based on the surface energies by using Materials Studio package. (b) The simulated equilibrium morphology of DFPHP molecules based on the surface energies by using Materials Studio package.