Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Fullerene Superlattices Containing Charge Transfer Complexes for Enhanced Nonlinear Optical Performance

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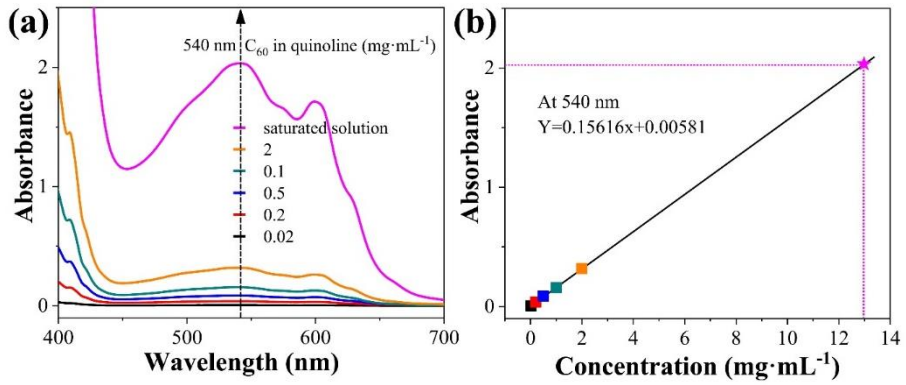

Fig. S1 a) UV-vis spectra of C_{60} in quinoline with exact concentrations and the supersaturated solution at unknown concentration, respectively. b) Linear fitting diagram of the concentration and absorbance at 540 nm for quinoline solutions of C_{60}. The concentration of the supersaturated solution was estimated based on its absorbance (marked with a pink asterisk).

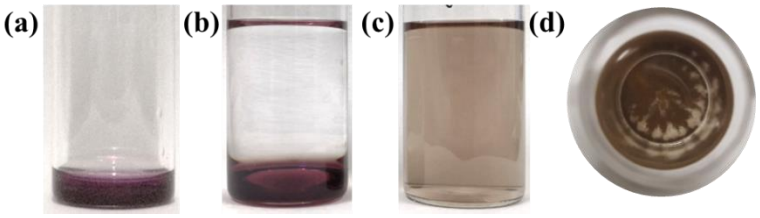

Fig. S2 Photos of the samples during the preparation of C_{60} microcrystals by LLIP method. (a) 1 mL C_{60} quinoline solution (2 mg·mL^{-1}) with 1 mL buffer layer (quinolone/alcohol, v/v=1:1) on the top. (b) The sample after slowly injecting 15 mL of poor solvent (EtOH in this case). (c) The sample after 1 h of incubation and 5 min of ultrasonication. (d) The sample after standing at 20 °C for 12 h where the microcrystals fully precipitated. Photos a-c are side views, while photo d is a top view.

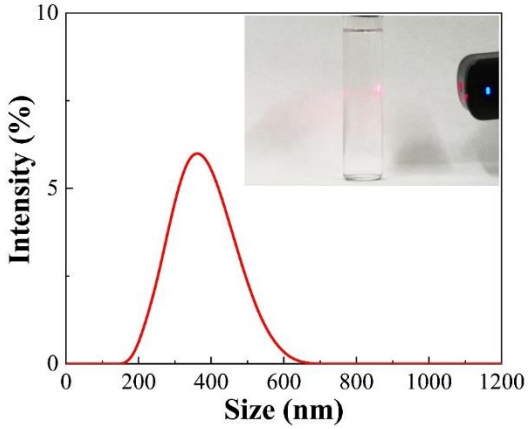

Fig. S3 DLS curve of the quinoline/MeOH mixture with the same volume ratio as that used for preparation of **HPH**. Inset is a photograph of the quinoline/MeOH mixture taken immediately after ultrasound, which shows Tyndall effect.

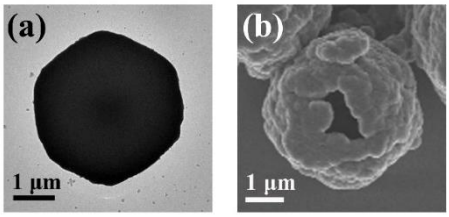

Fig. S4 a) TEM and b) SEM images of typical C_{60} superstructures obtained without ultrasound, which showed similar morphologies to **HPH**.

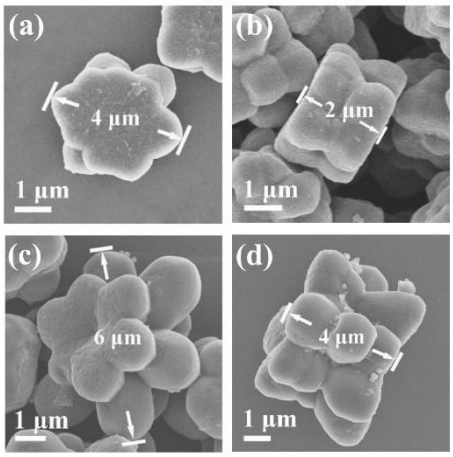

Fig. S5 SEM images of the C_{60} **MFs** prepared by adjusting the incubation time before ultrasonication to 0 h (a, b) and 2 h (c, d), respectively. Top view (a, c) and side view (b, d).

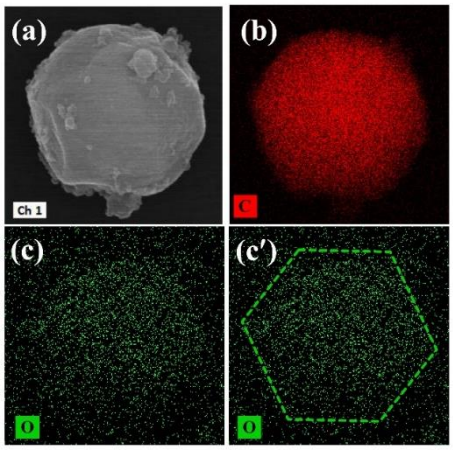

Fig. S6 SEM images with EDS mapping of a typical **HPH**. The polygon in panel c' is a guide for the eyes.

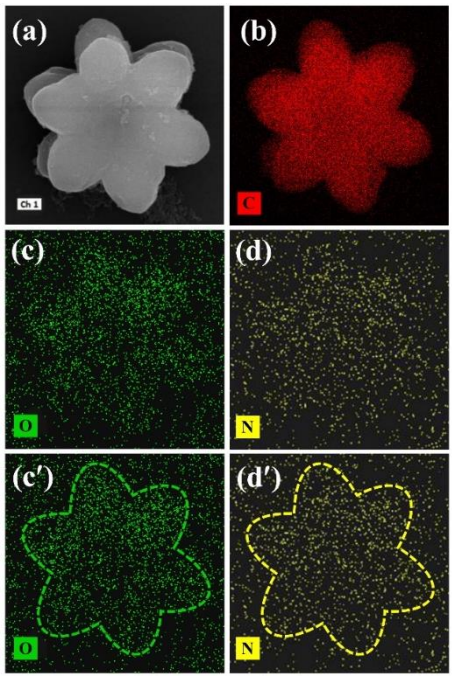

Fig. S7 SEM images with EDS mapping of a typical **MF**. The stars in panels c′ and d′ are guides for the eyes.

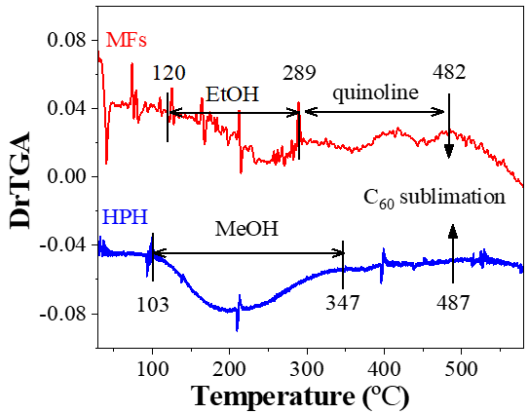

Fig. S8 DrTGA curves of **HPH** and **MFs.**

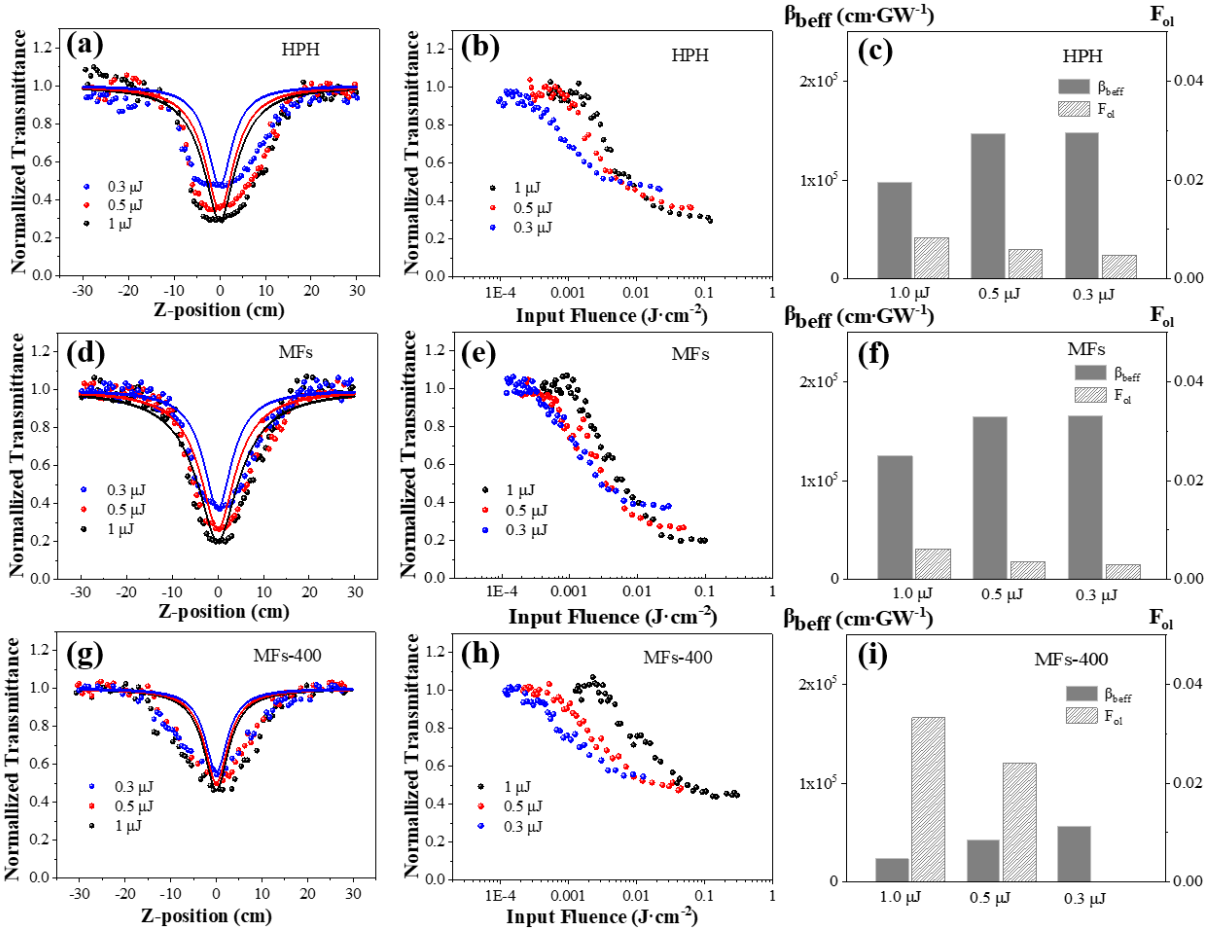

Fig.S9 Open aperture Z-scan curves (a, d, g), optical limiting responses (b, e, h) and statistics of β and F_{ol} (c, f, i) of the PMMA films containing 0.5 wt% of **HPH** (a-c), **MFs** (d-f), and **MFs-400** (g-i), respectively, obtained under 532 nm, 5 ns laser pulses with different energies as indicated. The solid lines in a, d, g depict theoretical fits.

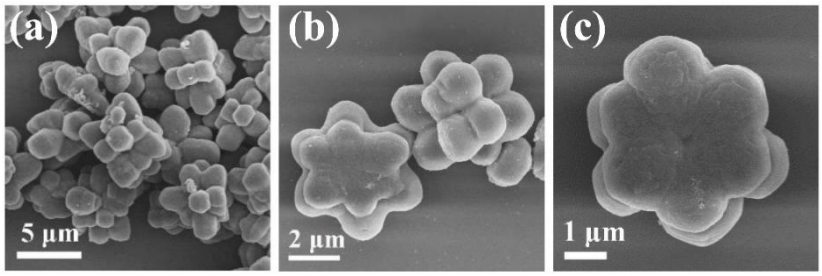

Fig. S10 SEM images with different magnifications of **MFs-400**.

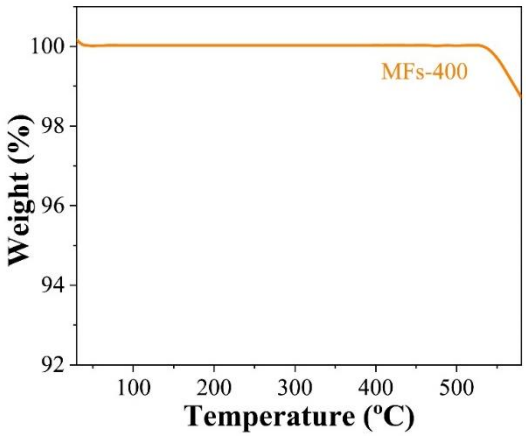

Fig. S11 TGA curve of **MFs-400**. Data from pristine C_{60} are also given for comparison.

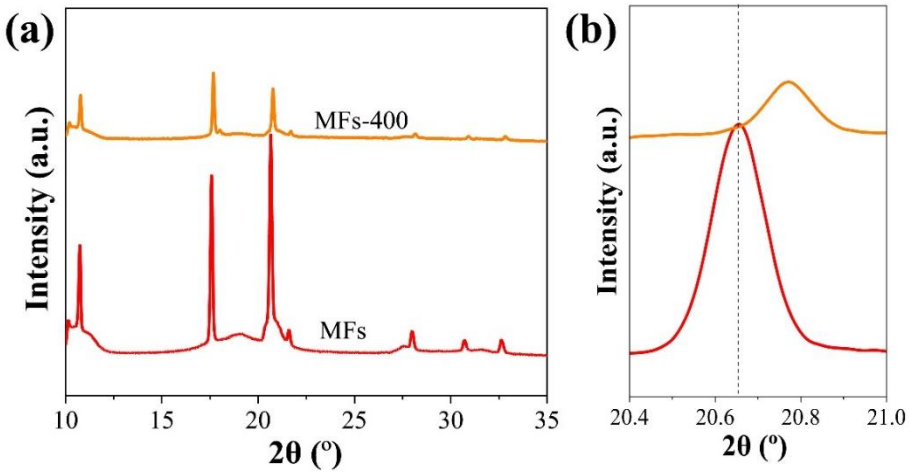

Fig.S12 a) XRD patterns of **MFs-400**. For comparison, data from **MFs** are also given. b) Magnified peaks of the (112) planes of the *hcp* lattices. The dashed line is a guide for the eyes.

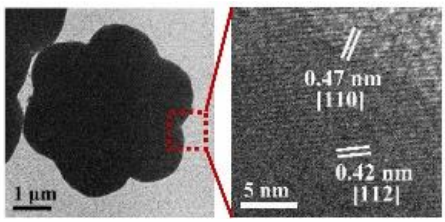

Fig. S13 TEM and HR-TEM images of **MFs-400**.

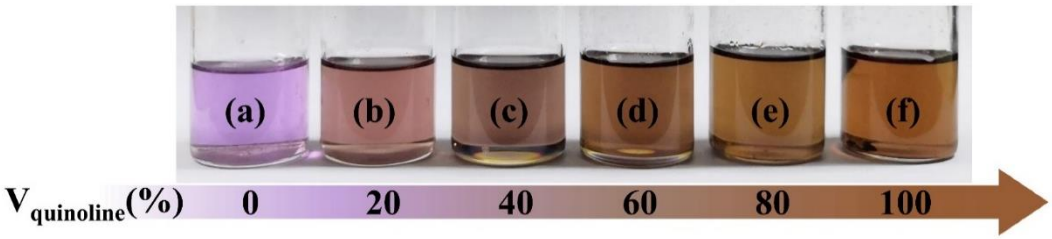

Fig. S14 The solvatochromic effect of 0.2 mg·mL^{-1} C_{60} in CH_2Cl_2/quinoline mixed solvent with a fixed total volume of 5 mL but varying volume percentage of quinoline. With the increase of the quinoline ratio (from left to right), the solution gradually changed from light purple to tan.

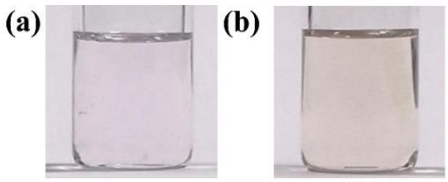

Fig. S15 Photos of diluted solutions from sample a (left) and sample f (right) in Fig. S14 by taking 200 μL of the stock solution and diluting with CH_2Cl_2 to 1 mL.

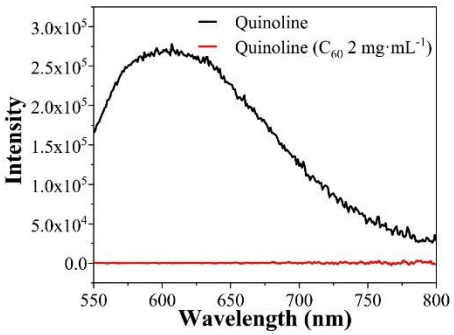

Fig. S16 Fluorescence spectra of quinoline before and after adding C_{60}. The wavelength of excitation is 532 nm and the slit width is 5 nm.

Table S1 Nonlinear absorption coefficient β and optical limiting value F_{ol} of some typical RSA materials at 532 nm.

β (cm·GW^{-1})	F_{ol} (J·cm^{-2})	Materials	Reference
11.9	\	TPhA-(C_{60})$_2$	*22*
1.4 × 10^{-12}	\	Penta(ZnP)C_{60}	*23*
\	~0.8	[60]fullerene containing dyads (porphyrin)	*24*
\	0.63	poly(C_{70}-Py) film	*27*
241.73	4.5	BP:C_{60} annealing	*46*
\	0. 25	C_{60}tpy-Ag	*49*
760	0.31	Modified [60]fullerene doped cholesteric	*50*
1.25 × 10^5	***0.00625***	***MFs (Multilayer flowers)***	***This work***

Table S2 Reduction potential versus Fc^+/Fc for 0.2 mg·mL^{-1} C_{60} in CH_2Cl_2/quinoline mixed solution with a fixed total volume of 5 mL (V_q represents the volume percentage of quinoline in the mixed solution).

	CV				DPV			
V_q (%)	E^1 red	E^2 red	E^3 red	E^4 red	E^1 red	E^2 red	E^3 red	E^4 red
0	**-0.664**	**-1.136**	**-1.544**	**-2.012**	**-0.407**	**-1.075**	**-1.499**	**-1.947**
20	**N/A**	**-1.141**	**-1.549**	**-2.031**	**N/A**	**-1.079**	**-1.507**	**-1.983**
40	**N/A**	**-1.145**	**-1.552**	**-2.039**	**N/A**	**-1.099**	**-1.518**	**-1.992**
60	**N/A**	**-1.167**	**-1.632**	**-2.075**	**N/A**	**-1.128**	**-1.542**	**-2.007**
80	**N/A**	**-1.180**	**-1.643**	**-2.087**	**N/A**	**-1.134**	**-1.547**	**-2.011**
100	**N/A**	**-1.195**	**-1.650**	**-2.100**	**N/A**	**-1.151**	**-1.601**	**-2.033**