## **Electronic Supplementary Information**

# Chiral organic photonics: self-assembled micro-resonators for enhanced circular dichroism effect in the non-linear optical signal<sup>†</sup>

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### **Experimental Section:**

#### 1. Materials:

(*R*, *S*) Binol, Bromine, Bromoethane, 4-fomyl phenyl boronic acid and  $Pd(PPh_3)_4$  were obtained from Aldrich. NaOH, K<sub>2</sub>CO<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> were purchased from Finar Chemicals Limited, Ahmadabad, India. Column chromatography was performed using Merck silicagel (particlesize 100-200 mesh). For UV-Vis and Flourescensce measurements HPLC grade solvents were used. Hexane, acetone, CHCl<sub>3</sub> and ethylacetate solvents were obtained from Hychem Laboroties, Hyderabad, India. All solvents were used after distillation.

#### 2. Instrumental Methods:

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy studies were performed on a Bruker DPX 500 spectrometer with solvent proton as an internal standard (CDCl<sub>3</sub>- $d_1$  = 7.26 ppm). UV-Visible absorption spectra were recorded on a SHIMADZU-UV-3600 UV-VIS-NIR Spectrophotometer. Size and morphology of the microspheres were examined by using a Zeiss field-emission scanninge lectron microscope (FESEM) operating at 3 kV. IR spectra were recorded on Nicolet 5700 FTIR or JASCO FT/IR 5300. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light.

#### 3. Single Particle Micro-Spectroscopy Studies :



Single particle micro-spectroscopy experiment was carried out on a back scattering mode setup of the Wi-Tec alpha 300 AR laser confocal optical microscope (T-LCOM) equipped with a Peltier-cooled CCD detector. 300 grooves/mm grating BLZ = 750 nm, with the accumulation time of 10 s and integration time of 1.0 s were used. Ten accumulations was performed for acquiring a single spectrum. A diode 405 nm laser was employed as an excitation source. A  $150 \times (0.95 \text{ NA})$  objective was used for the selective excitation of a single micro-sphere. Laser power was estimated using THOR Labs power meter.

#### 4. Syntheses of 1-S & 1-R: (1R or 1-S)-6,6'-Dibromo-2,2'-diethoxy-1,1'-binaphthalene

Compounds *R*-2 and *S*-2 were synthesized according to previous synthetic procedure.<sup>18 in the article.</sup>

To a 150 mL of dry round-bottomed flask was added *S*-2 or *R*-2 (100 mg, 0.201 mmol, 1 equiv.), 4-formyl phenyl boronic acid (67 mg, 0.442 mmol, 2.2 equiv.), K<sub>2</sub>CO<sub>3</sub> (0.82 g, 0.0012 mmol, 6 equiv.), tetrahydrofuran (10 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (34 mg, 0.0003 mmol, 0.15 equiv.), and H<sub>2</sub>O (4 mL). The flask was fitted with a water-cooled condenser, and the reaction mixture was heated to reflux at 80 °C for 24 h. The reaction mixture was cooled to 25 °C and extracted with ethylacetate (three times). The combined organic layers were washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The resulting residue was first subjected to silica gel flash column chromatography (40:60 ethylacetate/hexanes to 100% ethylacetate) to give the title compound (1-*R* or 1-*S*) as an off-white solid (60 mg, 62%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 10.06 (s, 2H), 8.17 (d, 2H), 8.07 (d, 2H), 7.98 (m, 4H), 7.87 (m, 4H), 7.54 (m, 4H), 7.28 (d, 2H), 4.13 (q, 4H), and 1.37 (s, 6H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) $\delta$ /ppm: 191, 155,

147, 134.9, 134.5, 133.9, 129.9, 129.2, 127.6, 126.7, 126.3, 125.4, 120, 116.2, 65.1, 30.9, and 15.0. FTIR (KBr;  $\bar{v}$  cm<sup>-1</sup>): 1698 (C=O), 2825 (OMe), and 2971 (C-H).



**Figure S1:** Absorption spectra: A) Aggregation behavior of **1-**R in THF upon addition of H<sub>2</sub>O and B) in different solvents.



Figure S2: Confocal microscopy (left) and FESEM (right) images of 1-R micro-spheres.



Figure S3: Single particle PL spectra of micro-spheres and the plot of FSR vs 1/D.



Figure S4: TPL spectra of 1-*R* in solution and micro-sphere states.

#### 6. NLO Experimental Setup:

For the investigations of NLO-CD and nonlinear absorption an experimental setup based on femtosecond (fs) Ti:Sapphire laser (pulse duration of 80 fs, 80 MHz, wavelength tuning range 740-860 nm) was used. The laser radiation was focused on the sample to a spot with the diameter of 50  $\mu$ m, and the laser beam polarization was controlled by the quarter-wave plate. In the NLO-CD experiments TPL radiation was spectrally selected by BG39 filter and detected by PMT. In the nonlinear absorption experiments I-scan technique was used. The radiation at the fundamental wavelength after passing through the sample as a function of the incident intensity was detected. Unlike the Z-scan, in the I-scan method the sample is kept at a fixed position and the illuminated area is kept constant during the measurements. The intensity of the laser radiation was varied continuously by rotating the gradient neutral density filter placed in the laser beam.

For the nonlinear absorption spectroscopy studies the sample was placed at the distance 0.85  $w_0$  from the lens focal plane, where  $w_0$  is the Rayleigh length. The required linear or circular polarization of the fundamental beam was selected by the necessary combination of half- and quarter-wave plates. Consequently, modulation of the intensity transmittance on the input power were measured, similar to shown in Fig. S5, for a definite fundamental wavelength and for the left- or right- circularly polarized laser beam.



**Figure S5:** A) Scheme of the I-scan method used for the determination of the TPA coefficient  $\beta$ . B) Dependence *T*(*I*) and the fit based on the function given in Eq-1.

In the nonlinear absorption spectroscopy studies, the TPA coefficient  $\beta$  was estimated from the TPA measurements carried out for different wavelength of the fundamental beam using the expression  $\alpha = \alpha_0 + \beta I$ , where  $\alpha$  is the total absorption coefficient, *I* is the incident light intensity and  $\alpha_0$  is the linear (intensity independent) absorption coefficient. Here the second summand corresponds to TPA. So the change in the beam intensity  $dI/dz = -(\alpha + \Delta \alpha)I$ ,  $\Delta \alpha = \beta I$ , or  $dI/dz = -\alpha I + \beta I^2$ , that is proportional to the intensity squared [B. Taheri et al., *Appl. Phys. Lett.* **68**, 1317 (1996); B. Taheri et al., *Optical Materials* **3**, 25, 1-255 (1994)]. Deviation of the experimental points from the linear dependence at higher incident power is associated with the role of higher-order nonlinearities contributing to the nonlinear absorption in that case.

The normalized transmission is given by the following expression:

$$T(I_0) = \sum_{n=0}^{\infty} \frac{\left[-\beta(1-R)L_{eff}\right]^n}{(n+1)^{3/2}} I_0^n,$$
 (Eq-1)

where  $L_{eff} = [1 - e^{-\alpha L}]/\alpha$  is the effective thickness of the sample, *R* is the reflectivity, L is the real thickness of the sample,  $\alpha$  is the single-photon absorption coefficient. The  $\beta$  value can be obtained by a numerical fit of the observed dependence of the transmission on the intensity.

#### 7. FDTD calculations:

In order to describe the observed spectral peaks in the photoluminescence spectra, we performed the calculations of the distribution of the electromagnetic field inside indivisual binol microspheres. The modeling is performed for the spheres with various diameters, from 1  $\mu$ m up to 8  $\mu$ m, the refractive index n=1.75 which corresponds to that of binol in this spectral range. Bellow results are shown for micro-spheres with diameter of 1.5  $\mu$ m. The modeling is performed using spherical symmetry of the system, with imposed periodical angular condition in the form of e<sup>imp</sup> factor for the fields, where *m* is the azimuthal mode number.

The simulation is made in the two steps: (1) we estimated the resonant frequencies of the electromagnetic field in a dielectric microsphere. This was done by introduction of a point dipole sources emitting a short Gaussian pulse are placed in near the inner surface of the sphere. The free evolution of the electromagnetic field was analyzed after the field source is switched off. This allowed to estimate the resonant wavelength typical for the microspheres in the visible spectral range by Fourier transform of the field. (2) After that, the field distribution of a particular mode is calculated when using a dipole source with resonance frequency (calculated on the first step) and a bandwidth considerably smaller than the free spectral range. This procedure is repeated for several appropriate mode numbers, m.

Various field distribution for different m values can be seen in Fig. S6. Resonant wavelengths for the spherical particles are degenerate with respect of m values, so different field distributions in microspheres correspond to the same resonant wavelength. At the same

time these resonances have approximately the same quality factors. It is demonstrated in columns in the Figure S6A for three neighboring resonant wavelengths. Electric field distribution of each field components for these three resonances are shown in Figure S6 B indicating TE and TM modes.



**Figure S6:** Distribution of the electromagnetic field of various angular modes *m* inside dielectric microspheres. Coordinate axes are common for all plots.



X-ray crystal structure data	
Chemical Formula	$C_{38}H_{30}O_4$
FW	550.21
Color	Light brown
Crystal System	Orthorhombic
Space group	$P_{21} P_{21} P_{21}$
а	8.273(5)
Ь	25.4125(18)
С	28.576(2)

α	90.00
β	90.00
Ŷ	90.00
V (Å)	6007.75
Ζ	4
ρ	1.153
Т	298 К
λ (Å)	0.71073
F (000)	2312
Theta	26.419
Index Ranges (h, k, l)	10, 31, 35
R1 (Reflections)	0.0787
Goodness of Fit on F <sup>2</sup> . S	1.784