Electronic Supplementary Information for

Chiral Macrocycle Induced Circularly Polarized Luminescence of a Twisted Intramolecular Charge Transfer Dye

Tiejun Li, [a,c] Hao Guo, [b,c] Yuan Wang, [a,c] Guanghui Ouyang,*[a] Qi-Qiang Wang[b] and Minghua Liu*[a,c]

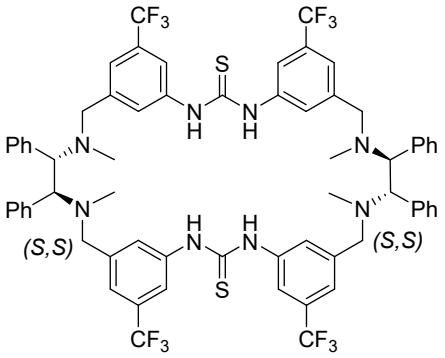
[a.] *Beijing National Laboratory for Molecular Science (BNLMS) and CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China.*

[b.] *BNLMS and CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China*

[c.] *University of Chinese Academy of Sciences, Beijing, 100049, China*

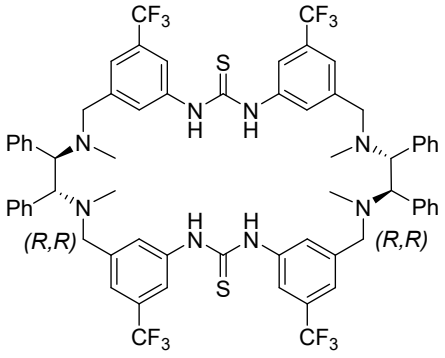
E-mail: ouyanggh@iccas.ac.cn, liumh@iccas.ac.cn.

1. Supplementary figures.



$C_{66}H_{60}F_{12}N_8S_2$
1257.36

M(*S*,*S*,*S*,*S*)



$C_{66}H_{60}F_{12}N_8S_2$
1257.36

M(*R*,*R*,*R*,*R*)

Scheme S1. The formula structures of (*S*, *S*, *S*, *S*)-macrocycle and (*R*, *R*, *R*, *R*)-macrocycle, which are abbreviated as ***S*-Host** and ***R*-Host**, respectively.

Table S1: Photophysical data of the host, guest dyes and their complexes.

	λ_{abs}/nm	ε_{max}/M^{-1} cm^{-1} (at λ_{abs})[a]	λ_{em} / nm	$\Delta\tilde{\nu}_{Stokes}$ / cm^{-1}	FLQY[b]	Lifetime /ns[c]
S-Host	280	3.27×10^4	317	4.2×10^3	0.5%	11.2
ANS-1	270	8.70×10^3	494	1.7×10^4	5.5%	9.0
Host/ANS-1[d]	278	5.95×10^4	464	1.4×10^4	16.1%	10.7
ANS-2	275	6.52×10^3	460	1.5×10^4	4.8%	10.9
Host/ANS-2[d]	254	4.47×10^4	412	1.5×10^4	2.1%	13.1

[a] The mole extinction coefficient is corresponding to λ_{abs}.
[b] The photoexcitation luminescent quantum yield is measured by absolute method using an integrating sphere.
[c] Diode laser excitation wavelength 260 nm, monitor emission wavelength decay at 460 nm, in THF, 298 K.
[d] 1:1 mole ratio in THF.

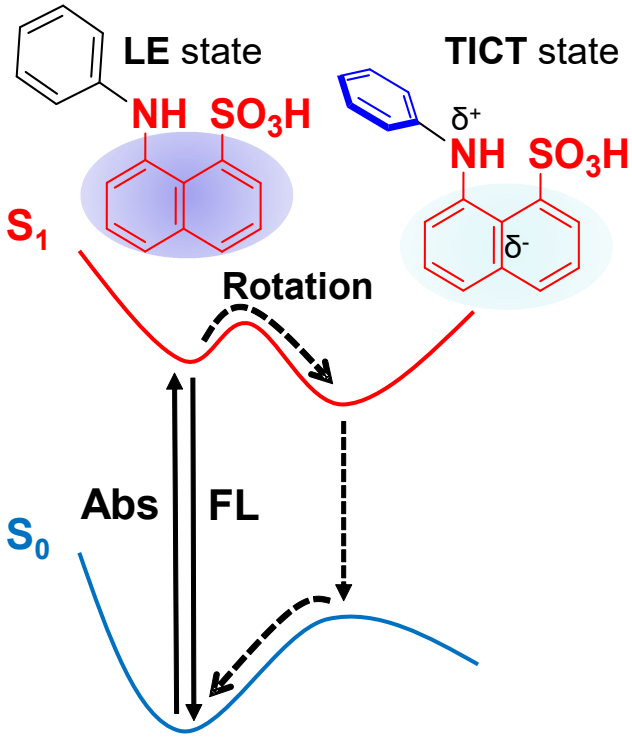


Figure S1. Schematic presentation of the LE state and TICT state conversion and fluorescence process in the TICT process of **ANS-1**.

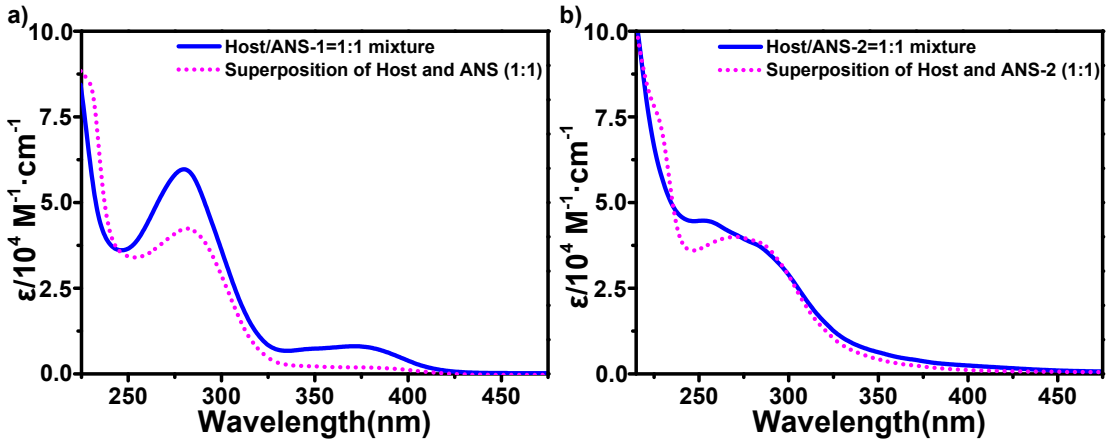


Figure S2. UV-Vis absorption spectra of a) ***S*-Host/ANS-1** mixture (1:1 in mole ratio, blue solid line), the superposition of individual ***S*-Host** and **ANS-1** absorption spectra (magenta dotted line). b) ***S*-Host/ANS-2** mixture (1:1 in mole ratio, blue solid line), the superposition of ***S*-Host** and **ANS-2** absorption spectra (magenta dotted line). [***S*-Host**] = [**ANS-1**] = [**ANS-2**] = 2×10^{-4} M in THF, 298 K.

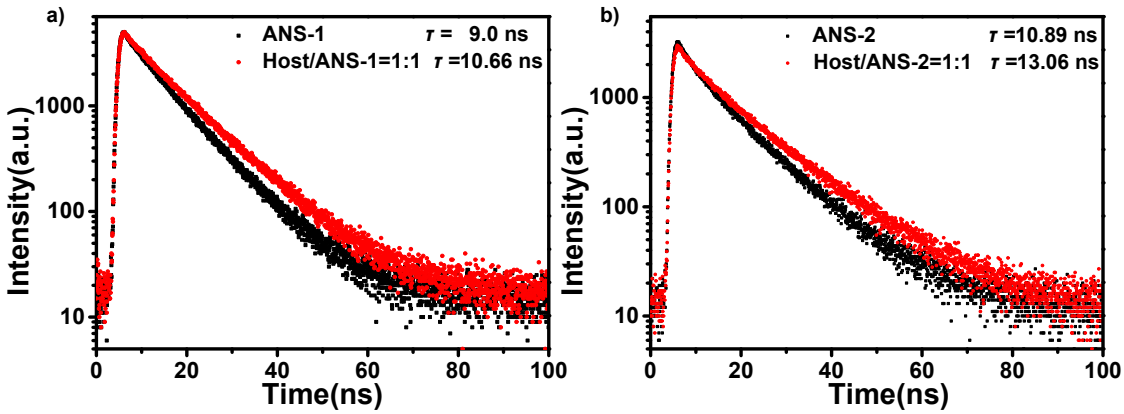


Figure S3. Emission decay curves of a) **ANS-1** (black dotted line) and the **Host/ANS-1** mixture (red dotted line). b) **ANS-2 (**black dotted line**)** and the **Host**/**ANS-2** mixture (red dotted line). [**Host**] = [**ANS-1**] = [**ANS-2**] = 2×10^{-4} M in THF, 298 K. λ_{ex} = 260 nm, monitor emission wavelength decay at 460 nm.

Table S2: Fitting data of emission decay curves.

	τ_1 (ns)	τ_2 (ns)	B_1	B_2	τ	χ^2
S-Host	3.4742	12.646	40.39%	59.61%	11.2	1.099
ANS-1	4.9890	9.4082	13.55%	86.45%	9.0	1.033
Host/ANS-1[d]	5.2477	10.9356	9.61%	90.39%	10.7	1.129
ANS-2	4.1546	11.3887	16.68%	83.32%	10.9	1.045
Host/ANS-2[d]	5.0082	13.5408	13.96%	86.04%	13.1	1.035

$$\tau = (B_1 * \tau_1^2 + B_2 * \tau_2^2)/(B_1 * \tau_1 + B_2 * \tau_2) \qquad \text{Eq. 1}$$

The emission decay curves are fitted by equation 1, where $\boldsymbol{\tau}$ represents the average lifetime, $\boldsymbol{\tau_1}$ and $\boldsymbol{\tau_2}$ represent lifetimes of different decay profiles, $\mathbf{B_1}$ and $\mathbf{B_2}$ represent proportion of each profile. χ^2 represents the confidence factor. When $0.8 < \chi^2 < 1.3$, the fitting result is reliable and applicable. And the closer the fitting value χ^2 is to 1, the better the fitting effect.

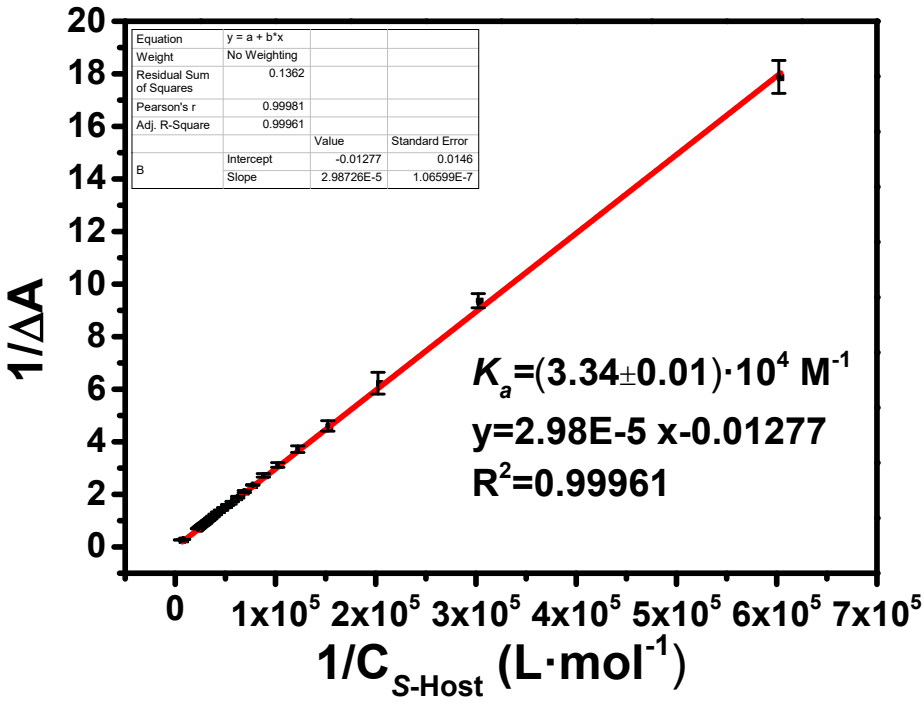


Figure S4. Benesi-Hildebrand equation shows a 1:1 binding model and the binding constant K_a = (3.34±0.01)×10^4 M^{-1} of the host-guest complex through titrating the ***S*-Host** into the TICT dye **ANS-1** (λ_{abs} = 280 nm).

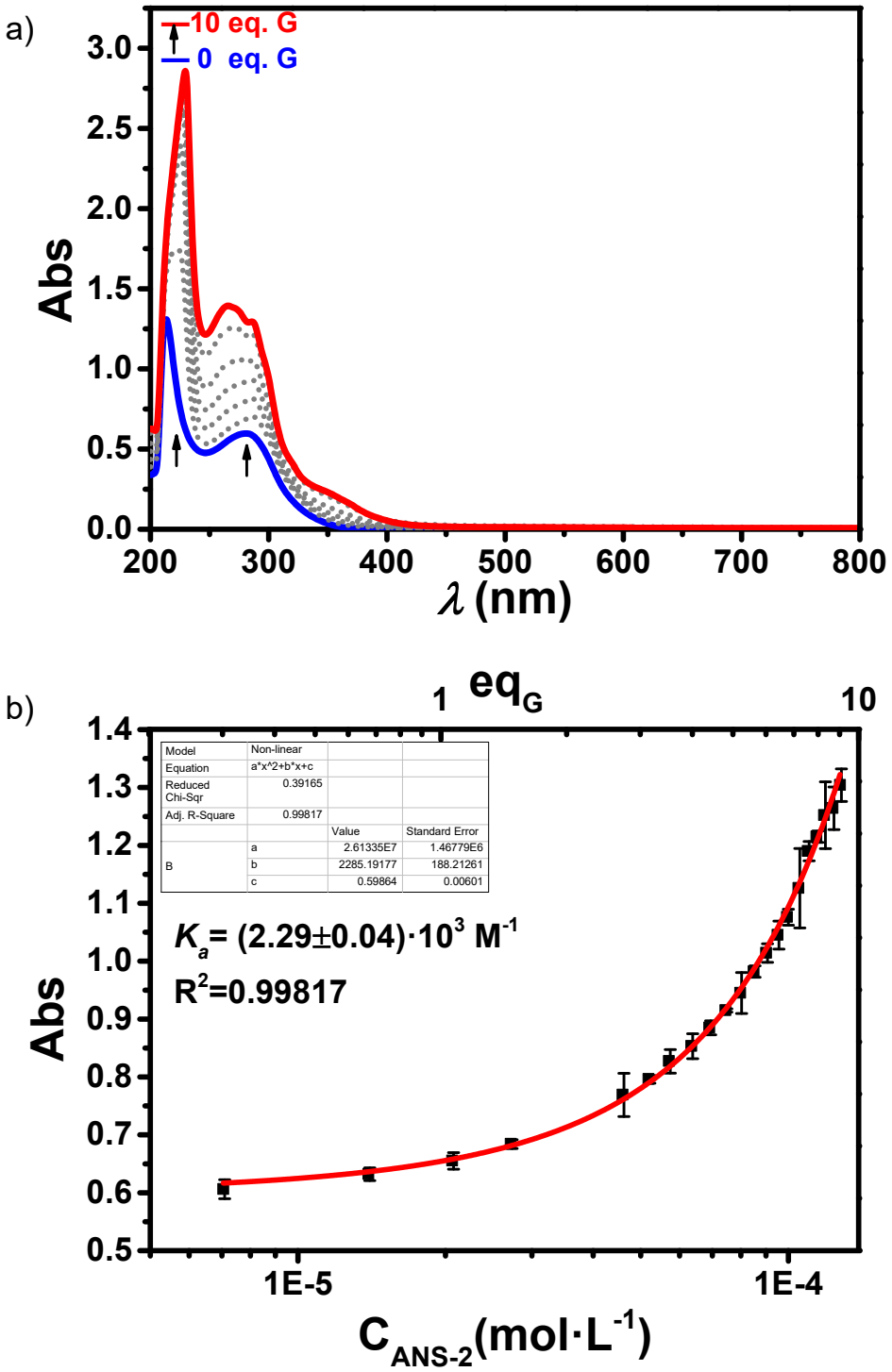


Figure S5. a) Isothermal UV/Vis binding titration of chiral-macrocycle **Host** upon addition of dye **ANS-2** at 298 K in THF (λ_{abs}=280 nm), the gray dotted lines are intermediate curves with increased amounts of **ANS-2**. b) Non-linear least-square curve fitting with 1:1 binding model and affords a constant of K_a = (2.29±0.04)×10^3 M^{-1} (λ_{abs} = 280 nm).

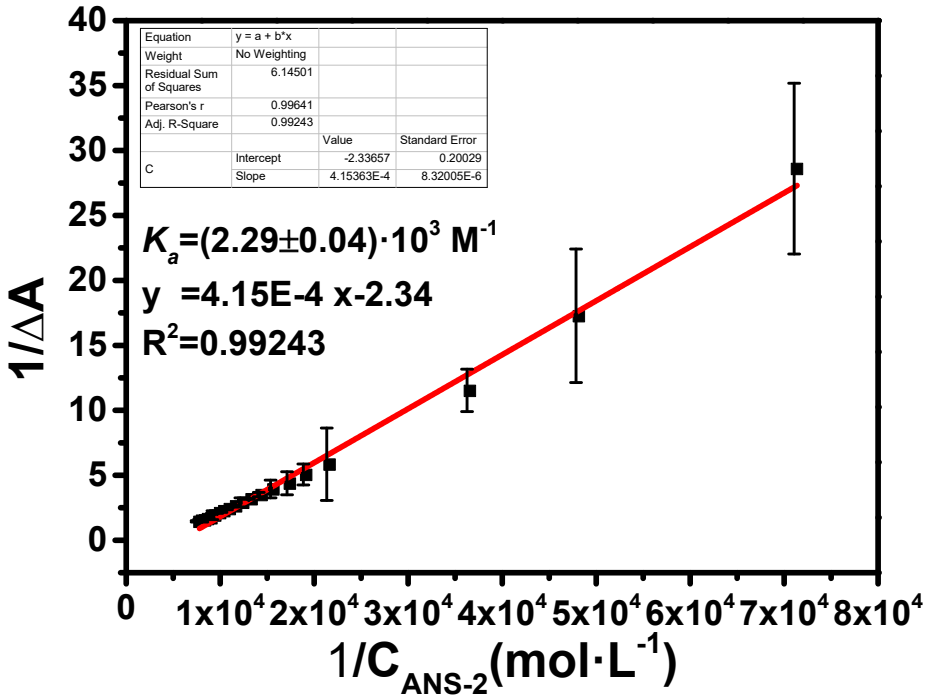


Figure S6. Benesi-Hildebrand equation shows a 1:1 binding model and the binding constant K_a = (2.29±0.04)×10^3 M^{-1} through titrating different equivalents of dyes **ANS-2** into the macrocycle **Host** (λ_{abs}=280 nm **)**.

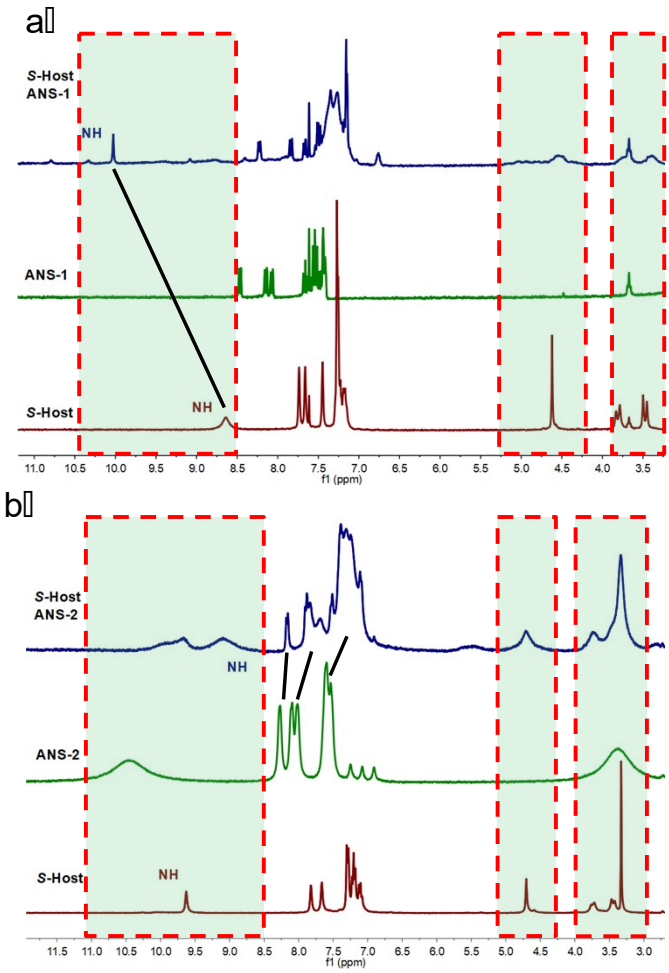


Figure S7. a) Stacked ^{1}H-NMR spectra (acetonitrile-d3, 300 MHz, 298 K) of ***S*-Host**, **ANS-1** and their host-guest complexes (1:1 in mole ratio). b) Stacked ^{1}H-NMR spectra (DMSO-d6, 300 MHz, 298 K) of ***S*-Host**, **ANS-2** and their host-guest complexes ***S*-Host/ANS-2** (1:1 in mole ratio).

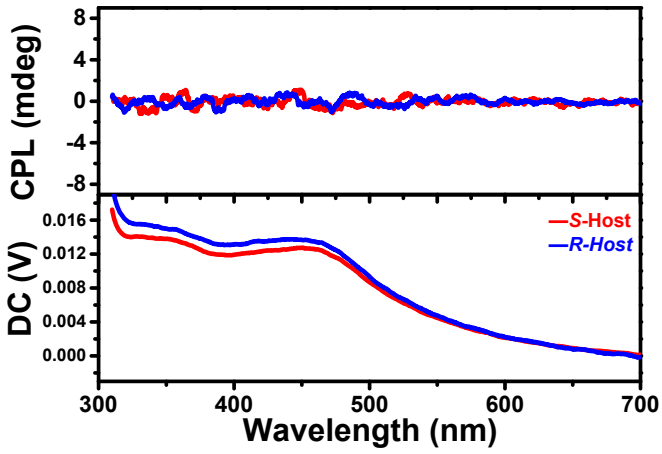


Figure S8. Circularly polarized luminescence spectra of ***R*-Host** (blue line) and ***S*-Host** (red line), the excitation wavelength λ_{ex} = 280 nm, [***R*/*S*-Host**] = 2×10^{-4} M in THF, 298 K.

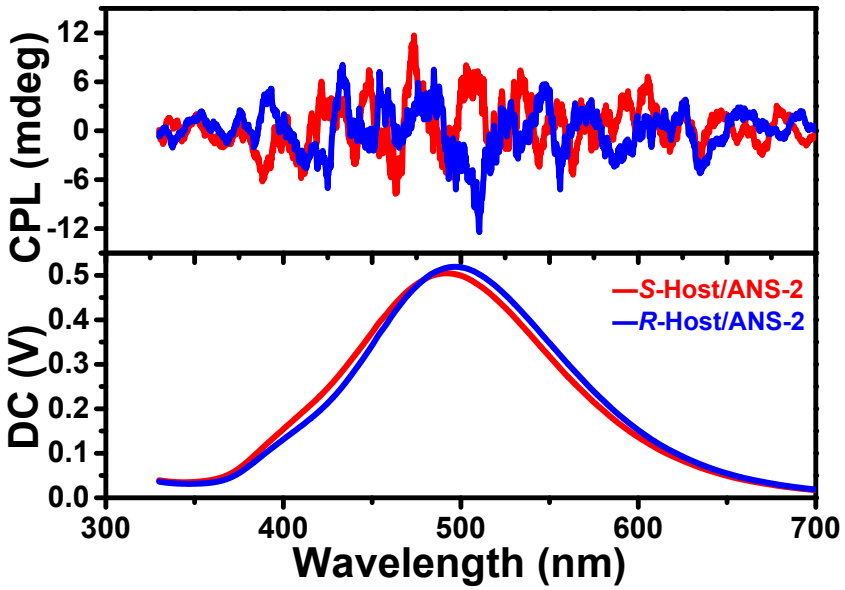


Figure S9. Circularly polarized luminescence spectra of ***R*-Host/ANS-2** mixture (blue line) and ***S*-Host/ANS-2** mixture (red line), the excitation wavelength λ_{ex} = 280 nm, [**Host/ANS-2**] = 2×10^{-4} M in THF, 298 K.

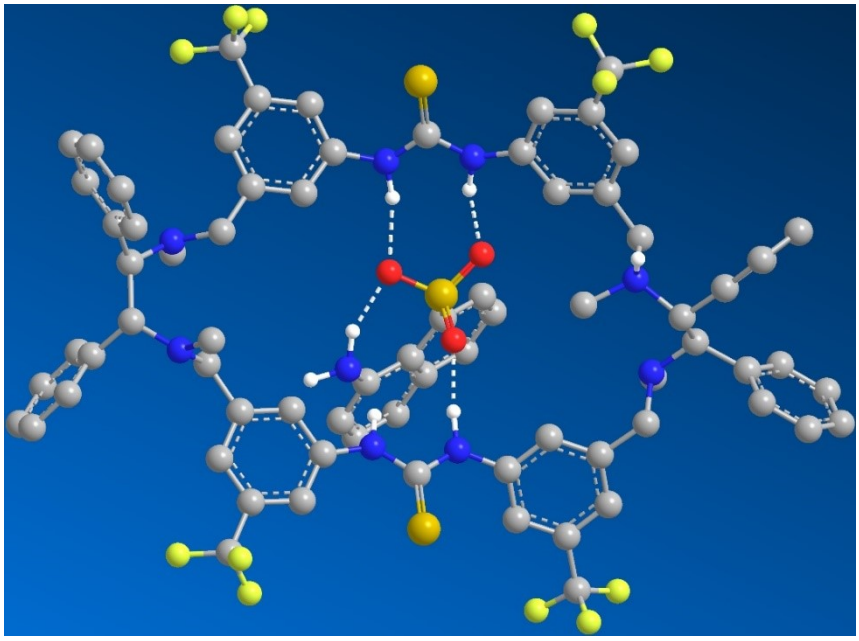
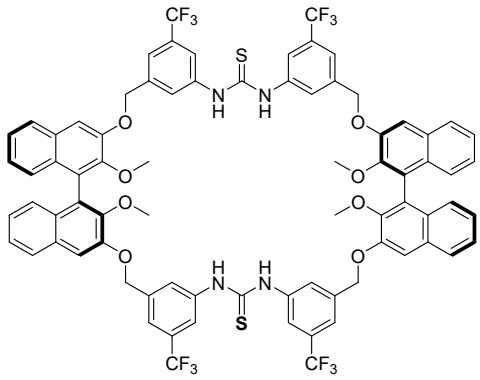
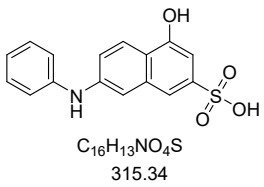


Figure S10. Proposed binding mode of ***S*-Host/ANS-2** complex based on energy-optimized structure by DFT method at Gaussian 09, B3LYP 6-31+G* level with a PCM model (solvent = tetrahydrofuran). The color balls represent: gray (carbon), white (hydrogen), blue (nitrogen), red (oxygen), green (fluorine) and brown (sulphur).





Scheme S2. The chemical structures of a binaphthol-urea macrocycle (M1) and a TICT-dye ANS-3.

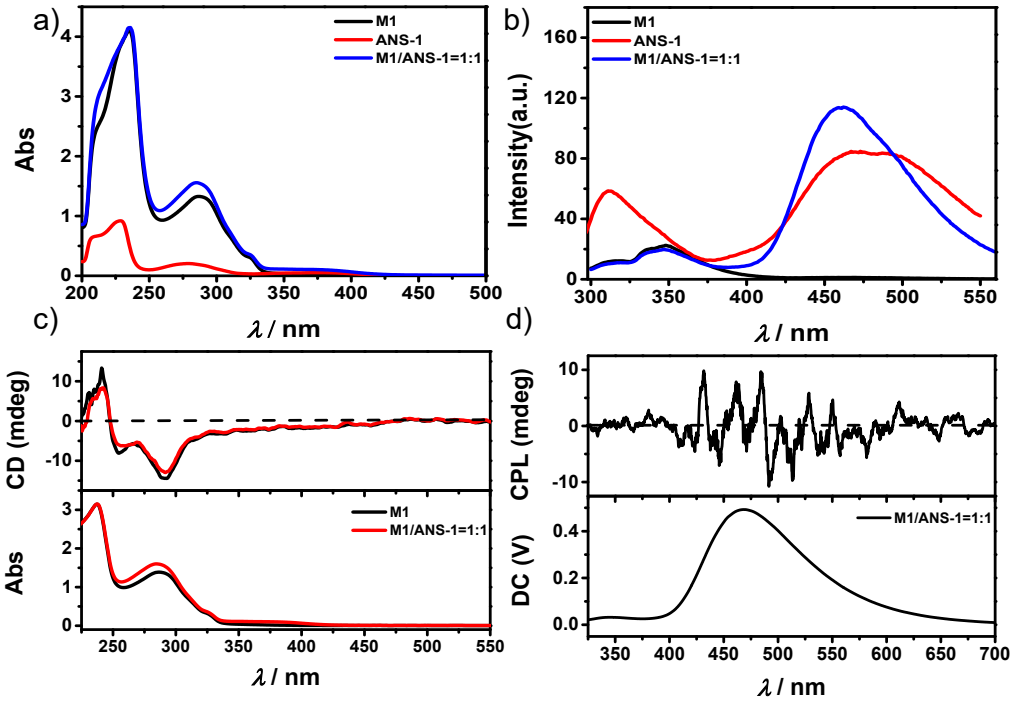


Figure S11. a) UV-Vis, b) FL, c) CD and d) CPL spectra of **M1**, ANS-1 and their mixture (1:1 in mole ratio). [**M1**] = [**ANS-1**] = 2×10^{-4} M in THF, 298 K.

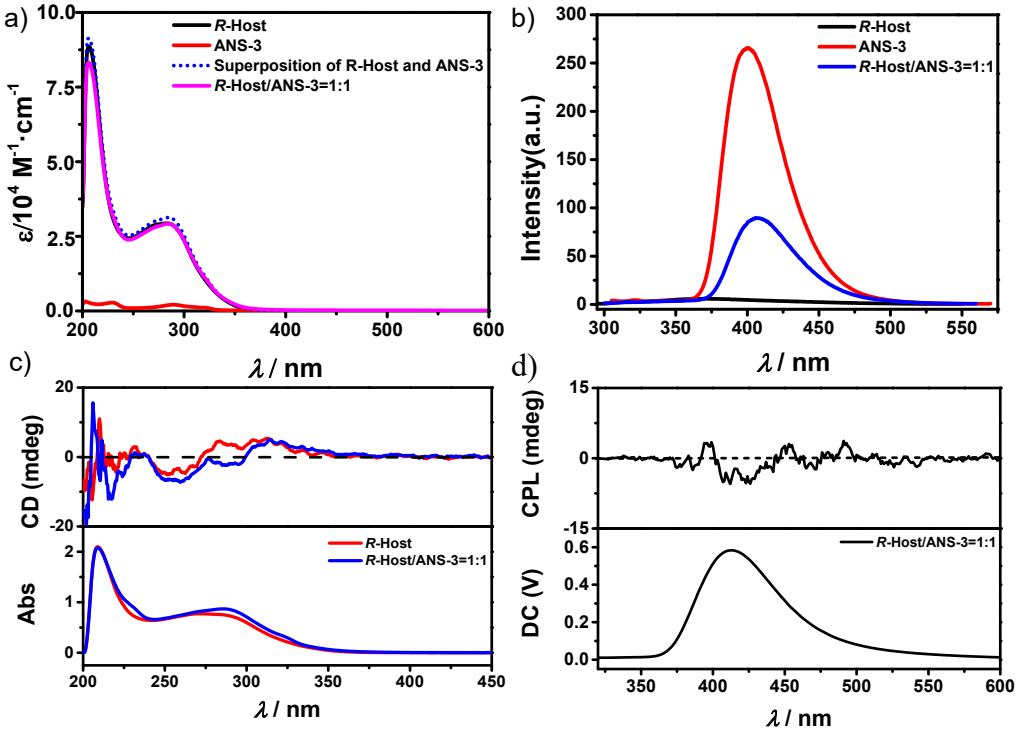


Figure S12. a) UV-Vis, b) FL, c) CD and d) CPL spectra of ***R*-Host**, ANS-3 and their mixture (1:1 in mole ratio). [***R*-Host**] = [**ANS-3**] = 2×10^{-4} M in THF, 298 K.

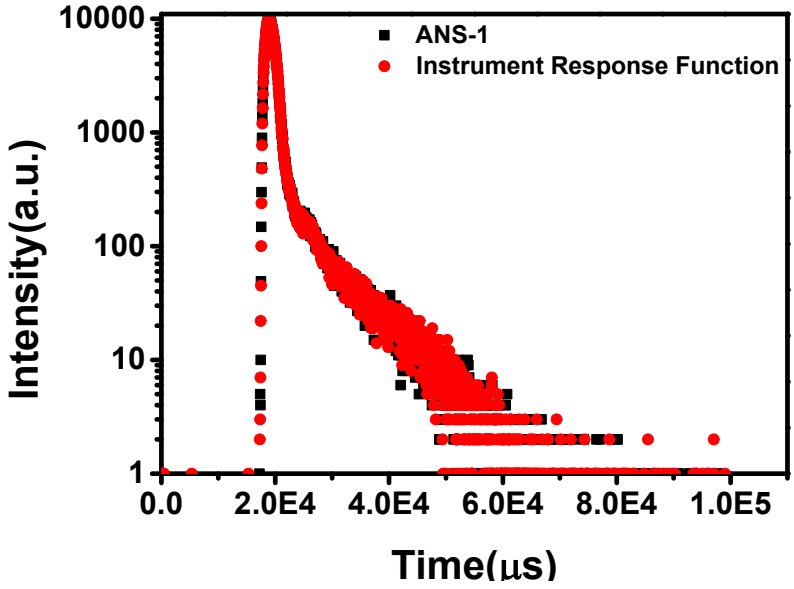


Figure S13. Luminescence lifetime measurements at longer time scale (μs) of **ANS-1**(black scatter) and instrument response function (IRF, red scatter).

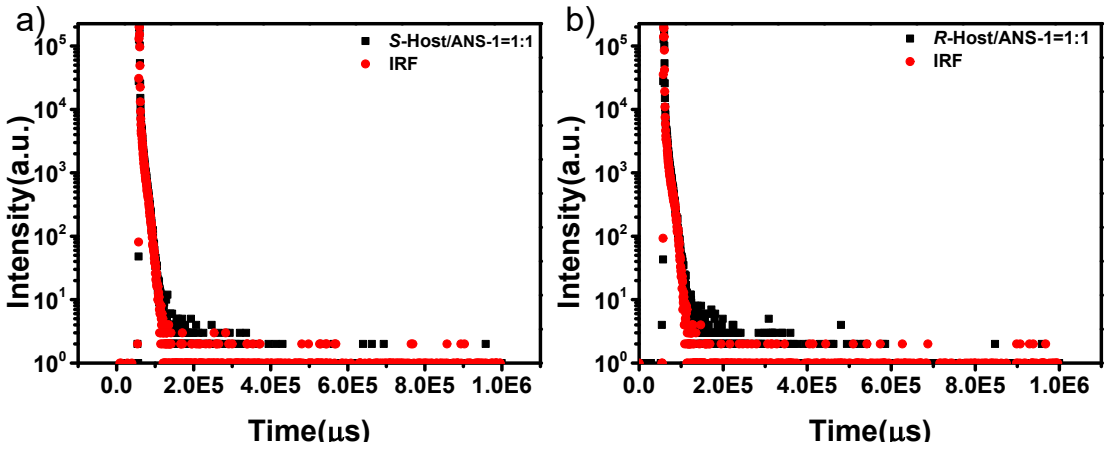


Figure S14. Luminescence lifetime measurements at longer time scale (μs) of a) ***S*-Host/ANS-1** = 1:1 mixture (black scatter), IRF (red scatter). b) ***R*-Host/ANS-1**=1:1 mixture (black scatter), IRF (red scatter). [**Host/ANS-1**] = 2×10^{-4} M in THF, 298 K.

2. General Information

All reagents and solvents were purchased from TCI and Aladdin and used directly without further purification. **ANS-1** (8-anilino-1-naphthalenesulfonic acid, > 95%, TCI), **ANS-2** (8-aminonaphthalene-1-sulphonic acid, ≥ 98.0% (HPLC), Aladdin).

Formation of the host-guest complex

Chiral macrocycle ***R*/*S*-Host**, dye 8-Anilino-1-naphthalenesulfonic acid (**ANS-1**) and 8-aminonaphthalene-1-sulphonic acid (**ANS-2**) were separately dissolved in organic solvent tetrahydrofuran at a concentration of 4×10^{-4} M. Equal volume of the host and guest solution were mixed and stirred for 30 min to give the corresponding host-guest complex with a concentration of 2×10^{-4} M.

Characterization Instruments and Methods.

UV−Vis spectra were recorded in cuvettes (path length 1 mm) on a SHIMADZU UV-2600 spectrometer. All the tested samples were prepared in tetrahydrofuran.

Fluorescence spectra tested samples were prepared in tetrahydrofuran at a concentration of 2×10^{-4} M on a HITACHIF-4600.

Circular Dichroism (CD) spectra were recorded in cuvettes (path length 1 mm) on a JASCO J-810 spectrophotometer.

CPL measurements were performed with a JASCO CPL-200 spectrometer. The DC values were adjusted to about 0.5 Voltage. For all the tested solution samples, the EX slit and EM slit were set as 5 nm, and the PMT voltage was set as 400 V.

Quantum yield were recorded with a HORIBA FluoroMax+.

Fluorescence lifetime were recorded with an Edinburgh FLS-980 photospectrometer.