Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

A racemate rules effect supramolecular polymer for ee determination of malic acids in the high ee region

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1. General

All commercial reagents and solvents were used as received.
^{1}H NMR spectra were recorded on a Varian MR400 NMR spectrometer and ^{13}C NMR spectra were recorded on an Agilent MR400 NMR spectrometer.
High-resolution mass spectra (HRMS) were taken on an Agilent 6530 HR ESI mass spectrometer.
Circular dichroism (CD) spectra were recorded on a Jasco J-815 CD spectropolarimeter, using a 1 cm quartz cuvette.

2. Molecular models of host-guest complexes

The dimeric PBI aggregates of **1** binding to Mal and **2** binding to Tar were modeled using molecular mechanics with the MMFFaq force field in Sparten 14'. To simplify the modeling, the substituent on one of the imide nitrogens of the PBI host was replaced with a methyl group.

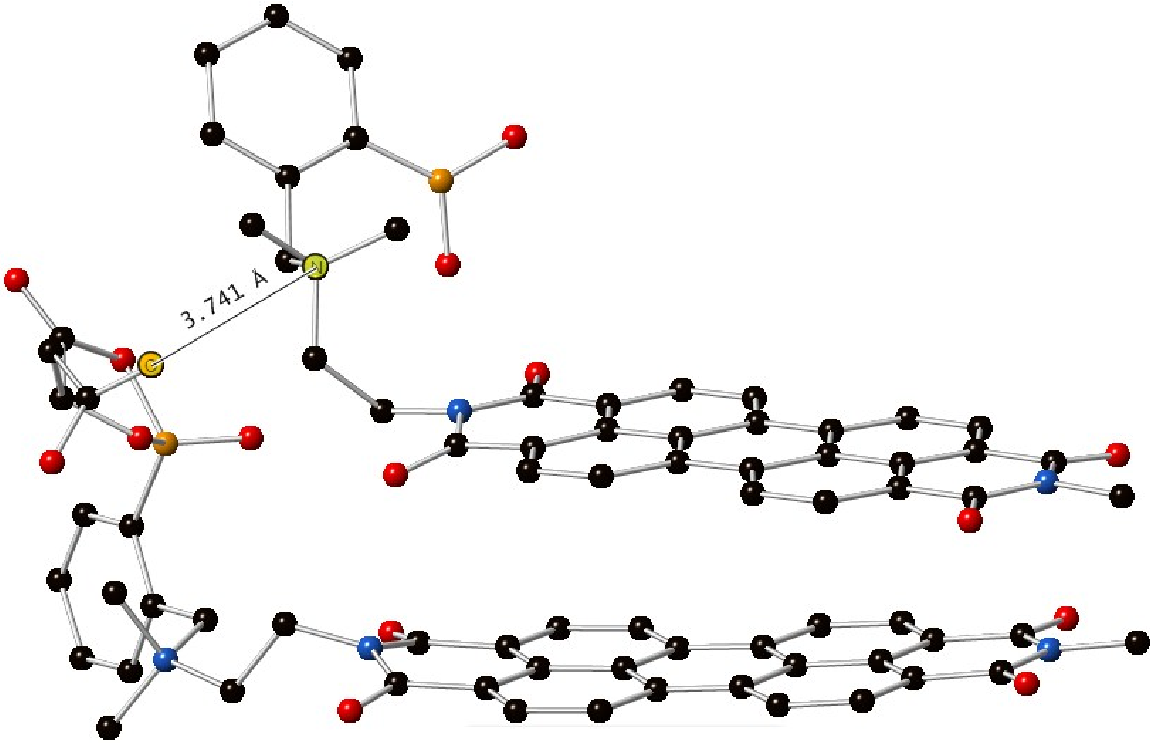


Fig. S1 Optimized structure of dimeric aggregate of **1** (with one of the imide substituents replaced by a methyl group) binding to L-Mal via a boronate ester linkage and a salt bridge (between a carboxylate group of Mal and a quaternary ammonium group of **1**, with an O···N distance of 3.7 Å as shown in the figure). Hydrogen atoms are omitted for clarity. The aggregate has a π–π distance of 3.8 Å. Atom colours: black, C; blue, N; red, O; and orange, B.

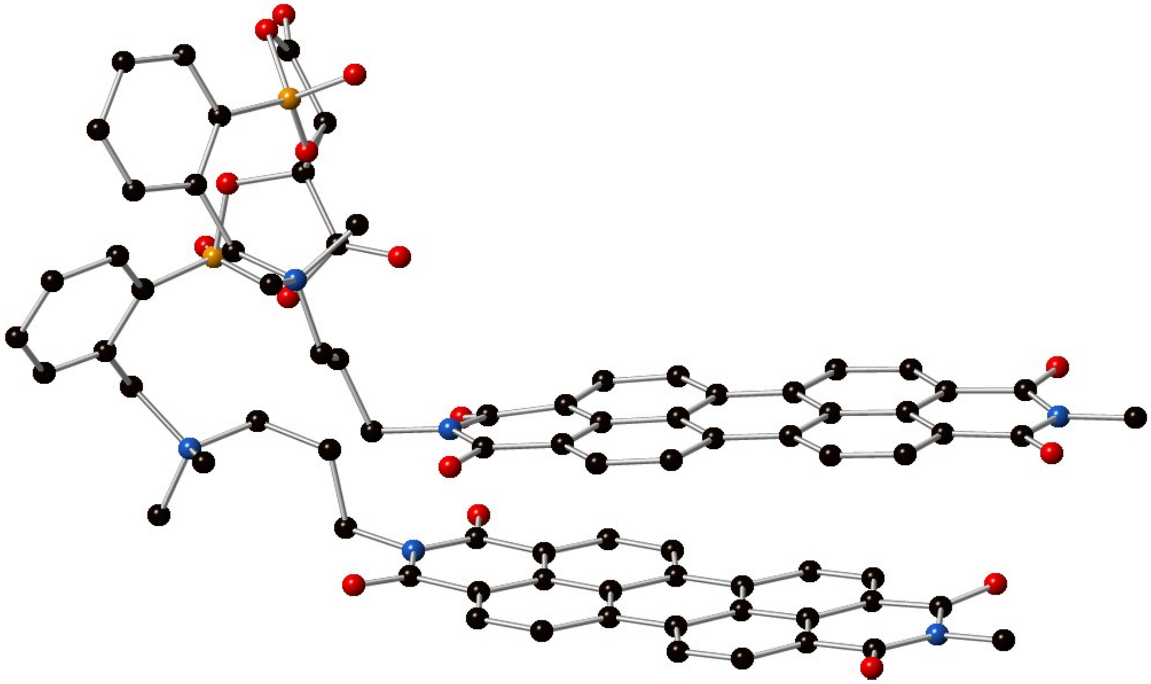
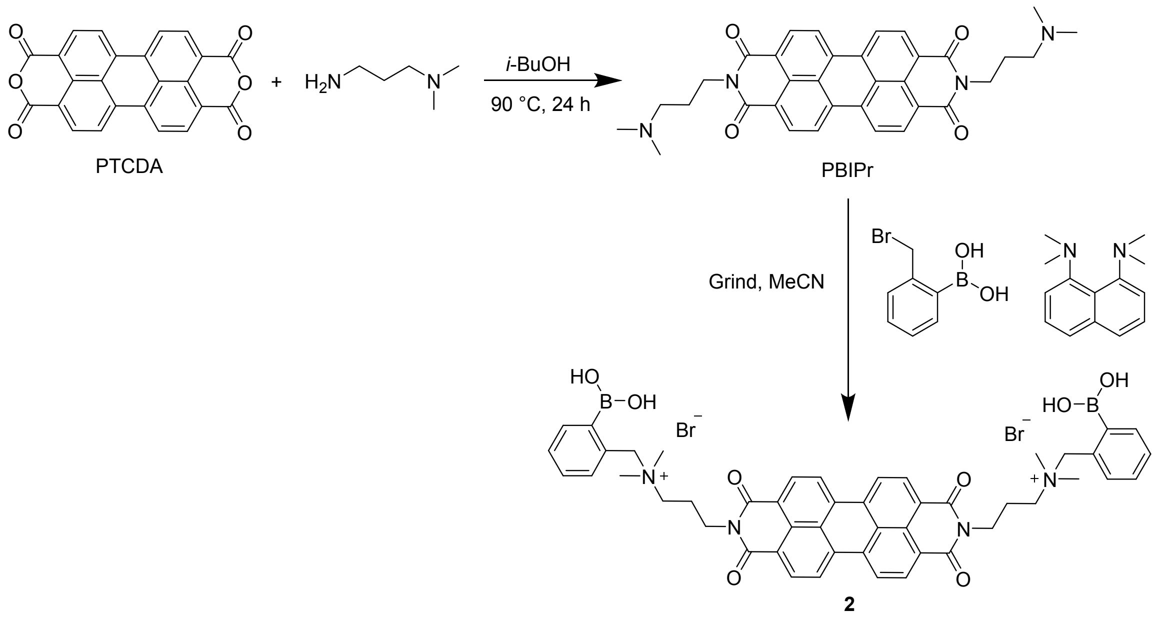


Fig. S2 Optimized structure of dimeric aggregate of **2** (with one of the imide substituents replaced by a methyl group) binding to L-Tar via two boronate ester linkages. Hydrogen atoms are omitted for clarity. The aggregate has a π–π distance of 3.8 Å. Atom colours: black, C; blue, N; red, O; and orange, B.

3. Experimental

3.1 Syntheses of Sensor 2



Sythesis of PBIPr

PBIPr was synthesized according to a reported procedure[1].

Synthesis of 2

PBIPr (0.112 g, 0.2 mmol), 2-bromomethylphenylboronic acid (0.108 g, 0.5 mmol), and 1,8-bis(dimethylamino)naphthalene (0.02 g, 0.1 mmol) was mixed and subject to grinding for 30 min, during which process several drops of MeCN was added to assist mixing. To the mixture was added 2-bromomethylphenylboronic acid (0.108 g, 0.5 mmol) and 1,8-bis(dimethylamino)naphthalene (0.02 g, 0.1 mmol) again, and the mixture was subject to further grinding for 30 min with several drops of MeCN. The resultant mixture was dissolved in hot methanol and the product was precipitated by adding Et2O after cooling. The red product **2** was collected and dried under vacuum (0.17 g, 86%). **^{1}H NMR** (400 MHz, TFA) 10.98 (d, J = 7.3 Hz, 4H), 10.92 (d, J = 7.1 Hz, 4H), 9.98 (s, 2H), 9.62 (d, J = 39.6 Hz, 6H), 7.02 (s, 4H), 6.53 (s, 4H), 5.75 (s, 4H), 5.16 (s, 12H), 4.59 (s, 4H).

HRMS(ESI-TOF) *m/z*: $[M + 2CH_3OH - 2H_2O]^{2+}$ Calcd for C50H52B2N4O8 429.1980; Found 429.2005.

Because of aggregation of **2** at high concentrations, ^{13}C NMR could not be obtained.

3.2 Sample preparation

The α-hydroxy carboxylate solutions with different ee were prepared by adding stock solutions of each enantiomer to the buffer (pH 5.0 50 mM acetate buffer). To 1.98 mL of the α-hydroxy carboxylate solutions was added 20 μL of 2.0 mM DMSO stock solution of **1** or **2**. The resultant host-guest solutions were immediately subject to CD measurements.

Determination of “unknown” ee

For each system, two five-point calibration curves were prepared for ee determination from 90% to 100% and from -90% to -100%, respectively. The “unknown” ee values were calculated using the calibration equations obtained from linear fit of the calibration curves.

Table S1 CD intensity of host-guest systems with "unknown" guest ee at the indicated wavelength. [Host] = 50 μM.

Host / guest, wavelength	CD intensity with different guest ee					
	92%	96%	98%	-94%	-96%	-98%
1 / Mal (0.3 mM), 487 nm	-53.6	-59.0	-60.7	57.4	60.0	62.5
1 / Lac (50 mM), 476 nm	-58.3	-58.4	-59.2	59.0	60.9	61.2
2 / Tar (30 μM), 487 nm	87.5	90.6	88.3	-83.9	-85.8	-85.9

3.3 CD spectra of 1/Lac, 2/Tar and 1/Mal complexes with different guest ee

3.3.1 1/Lac

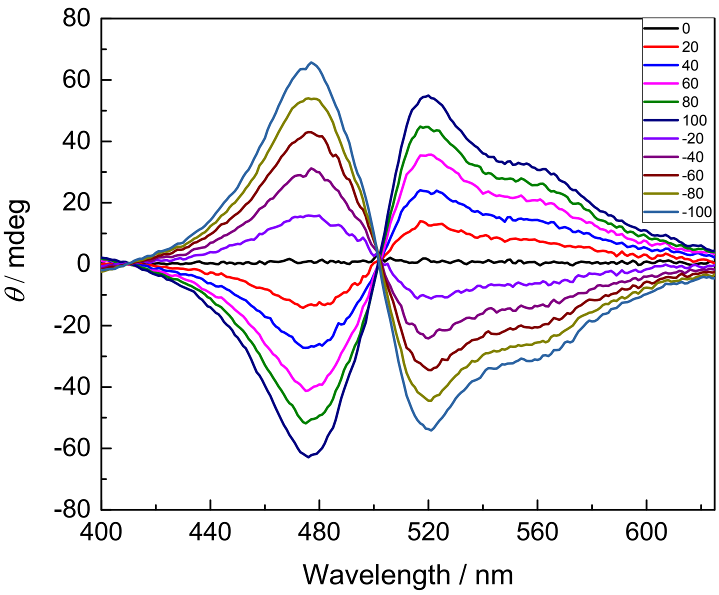


Fig. S3 CD spectra of the **1**/Lac complex with different ee of Lac in pH 5.0 acetate buffer. [**1**] = 50 μM, [L-Lac] + [D-Lac] = 50 mM.

3.3.2 2/Tar

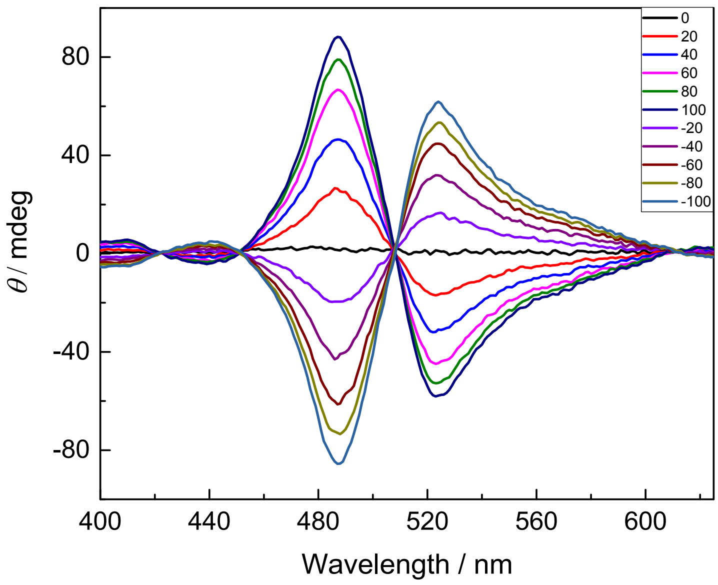


Fig. S4 CD spectra of the **1**/Tar complex with different ee of Tar in pH 5.0 acetate buffer. [**1**] = 50 μM, [L-Tar] + [D-Tar] = 30 μM.

3.3.3 1/Mal

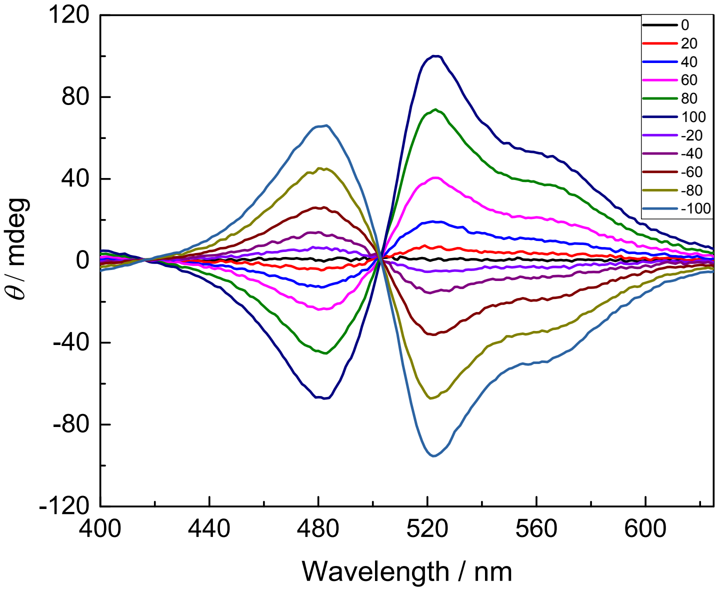


Fig. S5 CD spectra of the **1**/Mal complex with different ee of Mal in pH 5.0 acetate buffer. [**1**] = 50 μM, [L-Mal] + [D-Mal] = 0.3 mM.

3.4 Calibration curves for ee determination

3.4.1 1/Mal (RRE)

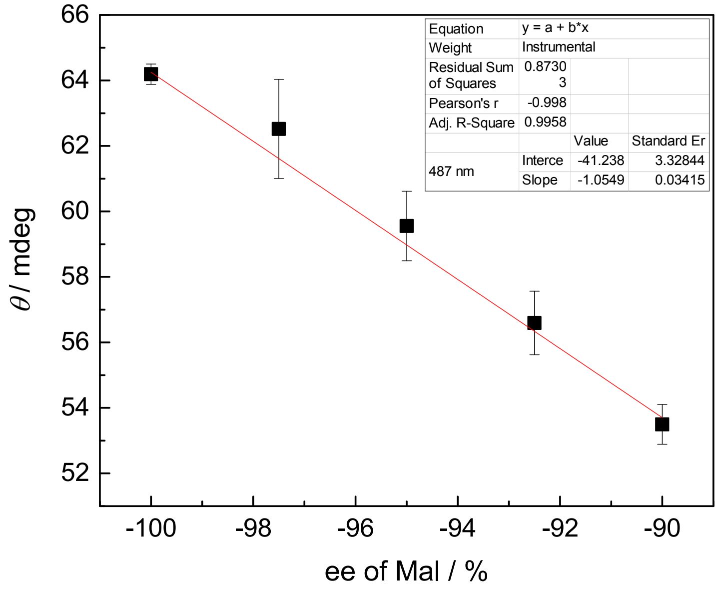


Fig. S6 Calibration curve for ee determination (-90% – -100%) of Mal using CD intensity of the **1**/Mal complex at 487 nm. [**1**] = 50 μM, [L-Mal] + [D-Mal] = 0.3 mM. Error bars represent standard deviations from three repeats.

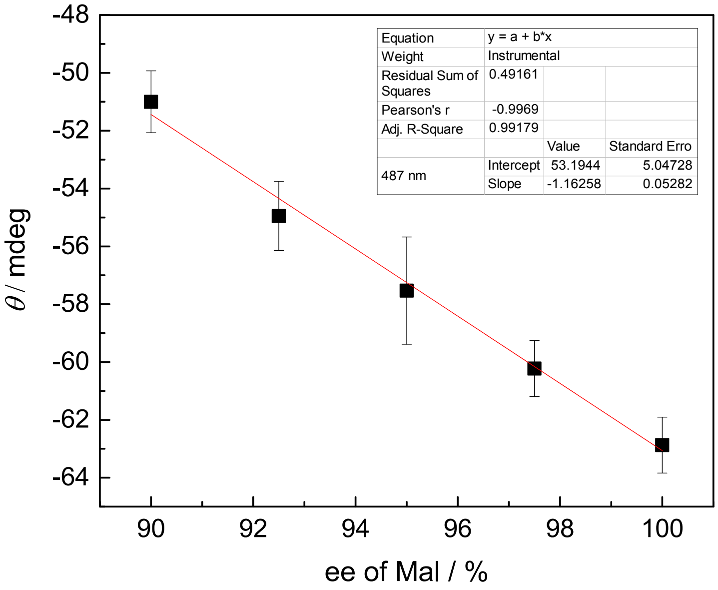
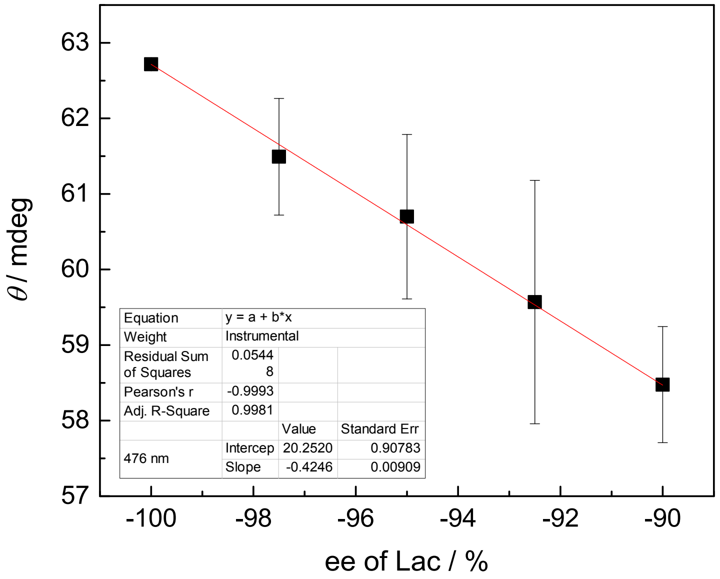


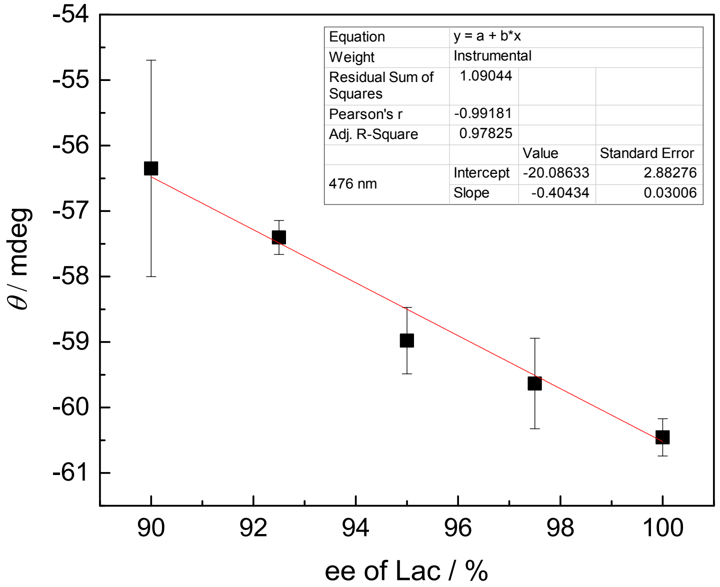
Fig. S7 Calibration curve for ee determination (90% – 100%) of Mal using CD intensity of the **1**/Mal complex at 487 nm. [**1**] = 50 μM, [L-Mal] + [D-Mal] = 0.3 mM. Error bars represent standard deviations from three repeats.

3.4.2 1/Lac (Linear)



Equation	y = a + b*x	
Weight	Instrumental	
Residual Sum of Squares	0.05448	
Pearson's r	-0.9993	
Adj. R-Square	0.9981	
	Value	Standard Err
476 nm Intercep	20.2520	0.90783
476 nm Slope	-0.4246	0.00909

Fig. S8 Calibration curve for ee determination (-90% – -100%) of Lac using CD intensity of the **1**/Lac complex at 476 nm. [**1**] = 50 µM, [L-Lac] + [D-Lac] = 50 mM. Error bars represent standard deviations from three repeats.



Equation	y = a + b*x	
Weight	Instrumental	
Residual Sum of Squares	1.09044	
Pearson's r	-0.99181	
Adj. R-Square	0.97825	
	Value	Standard Error
476 nm Intercept	-20.08633	2.88276
476 nm Slope	-0.40434	0.03006

Fig. S9 Calibration curve for ee determination (90% – 100%) of Lac using CD intensity of the **1**/Lac complex at 476 nm.. [**1**] = 50 µM, [L-Lac] + [D-Lac] = 50 mM. Error bars represent standard deviations from three repeats.

3.4.3 2/Tar (MRE)

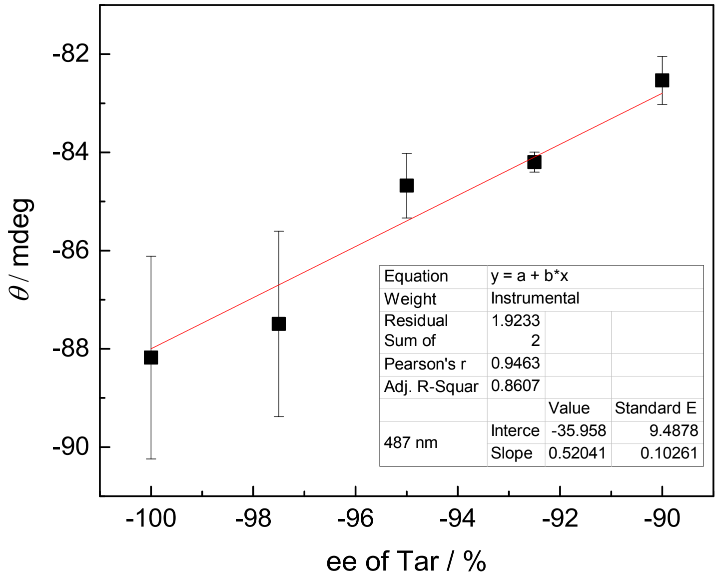


Fig. S10 Calibration curve for ee determination (-90% – -100%) of Tar using CD intensity of the **2**/Tar complex at 487 nm. [**2**] = 50 µM, [L-Tar] + [D-Tar] = 30 µM. Error bars represent standard deviations from three repeats.

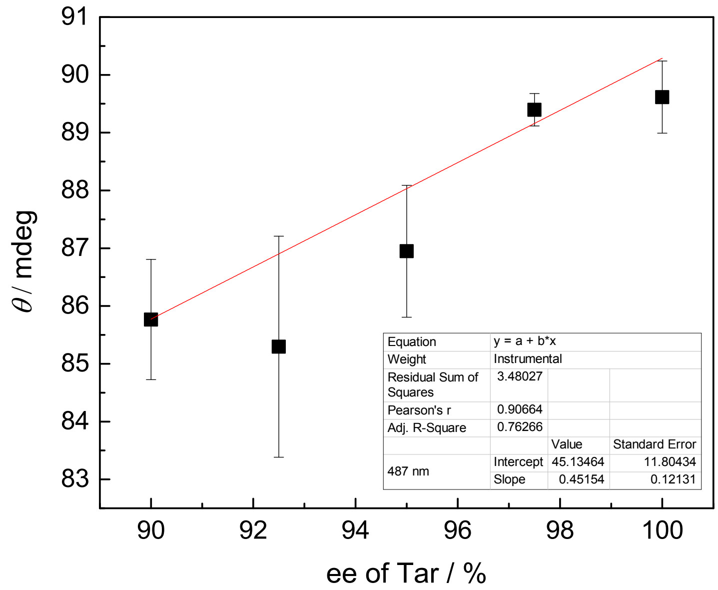


Fig. S11 Calibration curve for ee determination (90% – 100%) of Tar using CD intensity of the **2**/Tar complex at 487 nm. [**2**] = 50 µM, [L-Tar] + [D-Tar] = 30 µM. Error bars represent standard deviations from three repeats.

3.5 CD-ee titrations for the 1/Mal complex under different conditions

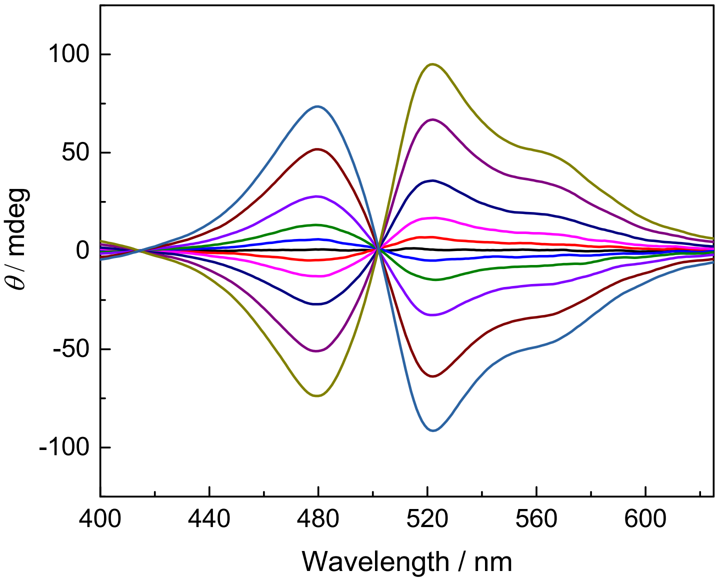


Fig. S12 CD spectra of the **1**/Mal complex with different ee of Mal in pH 5.5 50 mM MES buffer. [**1**] = 50 μM, [L-Mal] + [D-Mal] = 0.3 mM.

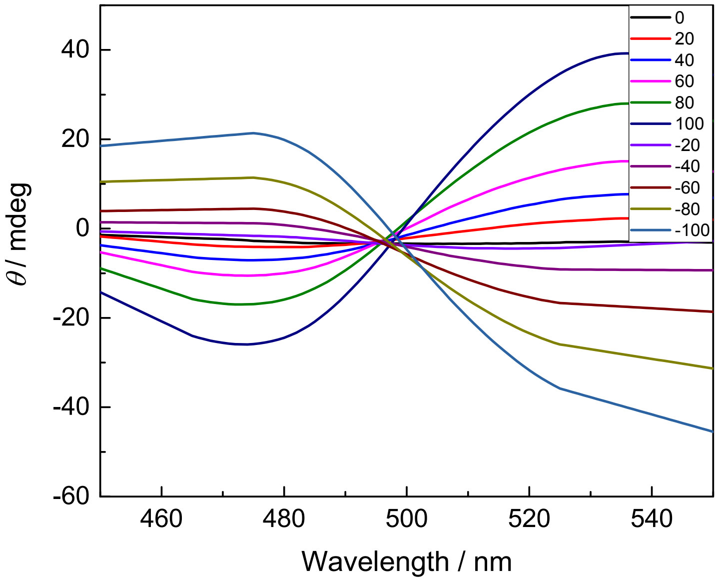


Fig. S13 CD spectra of the **1**/Mal complex with different ee of Mal in pH 5.0 acetate buffer containing 20% (v/v) MeOH. [**1**] = 50 μM, [L-Mal] + [D-Mal] = 0.3 mM.

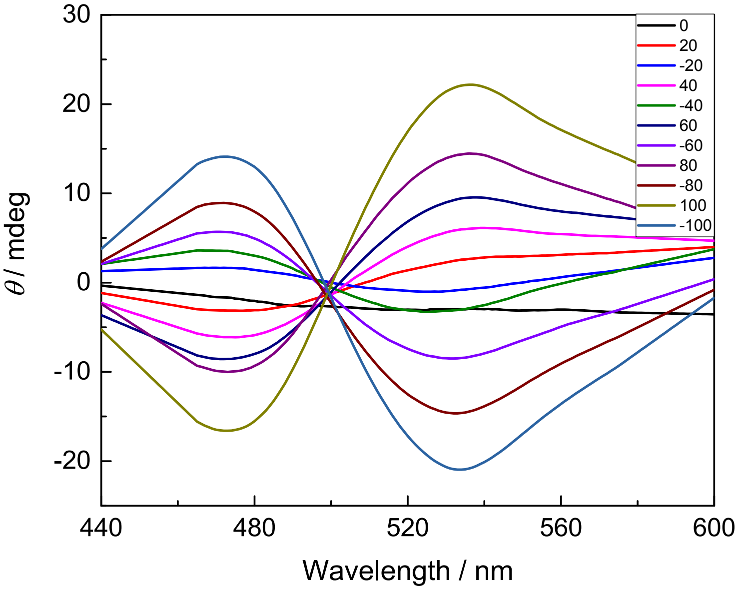


Fig. S14 CD spectra of the **1**/Mal complex with different ee of Mal in pH 5.0 acetate buffer in the presence of 1 M TMAO. [**1**] = 50 μM, [L-Mal] + [D-Mal] = 0.3 mM.

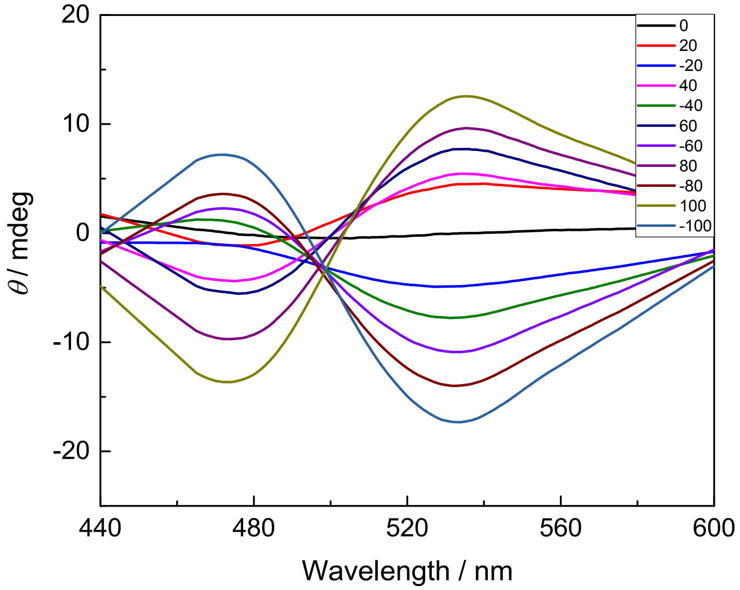


Fig. S15 CD spectra of the **1**/Mal complex with different ee of Mal in pH 5.0 acetate buffer in the presence of 1 M β-Ala. [**1**] = 50 μM, [L-Mal] + [D-Mal] = 0.3 mM.

Reference

1. J. Zhou, G. Yuan, J. Liu, C. G. Zhan, *Chem. Eur. J.*, 2007, **13**, 945-949.