Supporting Information

Barbier Polymerization Induced Emission of Cinnamaldehyde: A One-

Pot Grignard Reaction?

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Contents

Experimental details	
Materials	
Characterization methods	S3
Synthetic procedures	S4
Result characterization data	S6
Synthetic characterization	S7
Characterization of luminescent properties	S10
Artificial light-harvesting system experiments	S11
The detection of TNT	S12
Computational method	S13
Coordinate of optimized structures	\$14

Experimental details

Materials

THF was dried with sodium metal before use, and re-evaporated and purified with benzophenone as an indicator. Chemicals and other common reagents were obtained from commercial suppliers and used without further purification.

Characterization methods

Nuclear magnetic resonance (NMR) spectroscopy. The ¹H and ¹³C NMR measurements were performed on Bruker-BioSpin AVANCE III HD 400 spectrometer in CDCl₃ using tetramethylsilane as an internal standard.

Gel permeation chromatography (GPC). Number average molecular weight (M_n), Weight average molecular weight (M_w) and polydispersity indices (PDI) of the polymers were estimated on an Agilent 1260 Infinity II equipped with a G7110B isocratic pump and G7162A refractive index detector. Polystyrene standards were utilized, and DMF was used as the eluent at a flow rate of 1.0 mL/min at 50 °C.

Fourier transform infrared (FT-IR) spectroscopy. FT-IR Spectra using KBr pellets were recorded on a TENSOR II FTIR Spectrometre (Bruker, Germany). The spectra were recorded from an accumulation of 16 scans in the range of 4000-400 cm⁻¹ and were collected at room temperature. The OPUS v7.5 software auto-corrected the spectral base line and calculated the second derivative spectra.

UV-vis absorption spectra. The spectra were recorded in THF on a Shimadzu UV-2450 UV-Vis spectrophotometer at room temperature.

Luminescence spectroscopy. The spectrum was performed on a Shimadzu RF 5301pc fluorescence spectrophotometer in a quartz cuvette with a path length of 1 cm.

Field emission scanning electron microscope (FESEM) images. FE-SEM was performed with Hitachi 8100 operating at 5 kV and 10 μ A, respectively. Samples were prepared by placing a drop of mixture solution on single-side polished wafers.

Dynamic light scattering (DLS). DLS was performed with Brookhaven BI-200SM. Samples were prepared by 90% water/THF mixture solution.

Inductively coupled plasma spectrometer (ICP). ICP was performed with PerkinElmer optima 8000. Samples were digested in a nitrogen atmosphere at 800 °C, followed by ultrasound and filtration in 5 mL of deionized water to obtain the sample solution. The standard curve was obtained by configuring aqueous solutions of 0, 0.2, 0.4, 0.6, 0.8, and 1.0 ppm of magnesium chloride.

Gas Chromatograph (GC). GC data were recorded on Thermo TRACE 1300. Samples were prepared by taking out the reaction solution with different reaction times, dodecane as the internal standard.

Aggregation-induced emission (AIE) property. The measurements of the polymer in solvent/nonsolvent mixtures were tested. In this study, THF was selected as good solvent for polymers and water as aggregation-inducing nonsolvent. The luminescence spectra of polymers in THF/Water mixtures with different water content were recorded respectively on a Shimadzu RF-5301pc fluorescence spectrophotometer.

Artificial light-harvesting system property. The light harvesting systems were prepared by adding the mixtures of poly(α -isopropylhydrocinnamyl alcohol) (5.0 mg/mL in THF) with different amounts of NiR (1.0 mg/mL in THF) to a colorimeter followed by addition of the water. The spectra were recorded on the Shimadzu RF-5301pc fluorescence spectrophotometer.

The detection of 2,4,6-trinitrotoluene (TNT). The detection was performed by luminescence quenching of aggregated polymer in the THF/Water mixtures. The luminescence spectra (excitation @ 470 nm) of poly(α -isopropylhydrocinnamyl alcohol) solution (0.3 mg/mL in water/THF mixtures with 90% water fractions (vol%)) upon addition of different amounts of TNT were tested. Thus, the intensities and quenching ratio (the luminescence quenching efficiency = (1- I/I₀) ×100%, I and I₀ denote the luminescence intensity of poly(α -isopropylhydrocinnamyl alcohol) with and without TNT, respectively) of poly(α -isopropylhydrocinnamyl alcohol) solution upon addition of different amounts of TNT were acquired. Take the poly(α -isopropylhydrocinnamyl alcohol) solution upon addition of different amounts of the prepared test paper.

Synthetic procedures

Synthesis of poly(α-isopropylhydrocinnamyl alcohol). In a flame-dried Schlenk tube containing freshly peeled Mg scraps (0.27 g, 1.5 equivalent) under a nitrogen atmosphere, add 5 mL THF, trans-Cinnamaldehyde (1.00 g, 1.0 equivalent), 2-Chloropropane (0.65 g, 1.1 equivalent) and 0.1 mL of 1, 2-dibromoethane as activator through a syringe at room temperature, then move to an 80 °C oil bath. After reaction for 15 min, the solution was quenching and hydrolysis with 20 mL saturated aqueous ammonium chloride. After filtration and workup with dichloromethane / water, the organic solution was dried with anhydrous MgSO₄ and concentrated under reduced pressure. After the product was purified by precipitation into excessive petroleum ether, filtered and dried under vacuum, 1.01g poly(α-isopropylhydrocinnamyl alcohol) was obtained as a yellow powder with a yield of 75.9%. ¹H NMR (400 MHz, CDCl₃): δ =6.82-7.72 (broad, -C₆H₅-), 1.54-3.72 (broad, -CH-), 1.13-1.33 (broad, -OH), 0.60-1.02 (broad, -CH₃).

Synthesis of 4-methyl-1-phenylpent-1-en-3-ol. To one flame-dried Schlenk tube was added trans-Cinnamaldehyde (1.0 g, 1.0 equivalent) dissolved in THF (5 mL) through a syringe, and isopropylmagnesium chloride (1.5 eq) was slowly added dropwise to the Schlenk tube under ice-water bath. After 12 hours of reaction, the reaction was quenched with distilled water and extracted three times with dichloromethane. The organic phases were combined and dried with anhydrous MgSO₄. Then the solvent was removed by rotary evaporation under vacuum and the residue was chromatographed on silica gel (petroleum ether/ethyl acetate = 30:1) to yield 4-methyl-1-phenylpent-1-en-3-ol (1.0g, 75.2%). ¹H NMR (400 MHz, CDCl3): δ=7.39-7.21(m, 5H), 6.58(d, 1H), 6.25(dd, 1H), 4.03(t, 1H), 1.85(m, 1H), 1.79(s, 1H), 0.99(dd, 6H). ¹³C NMR (100 MHz, CDCl3): δ =136.91(Cd), 131.26(Ce), 130.96(Cf), 128.68(Ca), 127.69(Cb), 126.55(Cc), 78.24(Cg), 33.71(Ch), 18.41 and 18.21(Ci).

Result characterization data

Entry	T °C	THF (mL)	b (eq)	t (h)	Yield ^a (%)	М _п ь	M _w /M _n ^b
1	45	5	1.2	24	39.5	4800	1.43
2	60	5	1.2	24	44.2	5500	1.12
3	80	5	1.2	24	65.5	5500	1.13
4	80	2	1.2	24	56.7	5600	1.12
5	80	8	1.2	24	56.1	5400	1.12
6	80	5	1.1	24	78.2	6100	1.13
7	80	5	1.0	24	60.1	5500	1.10
8	80	5	0.5	24	43.6	5900	1.16
9	80	5	0.1	24	12.8	5100	1.13
10	80	5	1.1	1.0	77.7	6100	1.15
11	80	5	1.1	15min	75.9	6100	1.14
12 ^c	80	5	1.1	24	15.0		
13 ^d	80	5	1.1	24	59.4	4900	1.10

Table S1 Results of Barbier polymerization of cinnamaldehyde

^a Isolated yield; ^b Measured by GPC; ^c Switch from isopropyl chloride to isopropyl bromide; ^d Replace 1,2-dibromoethane with iodine

Synthetic characterization



Fig. S1 Grignard reaction between isopropyl Grignard reagent and cinnamaldehyde and the ¹H (400 MHz) NMR and ¹³C (100 MHz) NMR spectrum of reaction product in CDCl₃.



Fig. S2 Characterizations of poly(α -isopropylhydrocinnamyl alcohol) prepared with iodine activator. (A) ¹H NMR spectrum of poly(α -isopropylhydrocinnamyl alcohol) in CDCl₃, and (B) GPC curve of poly(α -isopropylhydrocinnamyl alcohol) in DMF.



Fig. S3 Characterizations of poly(α -isopropylhydrocinnamyl alcohol). (A1) ¹H NMR spectra of 2-Chloropropane, (A2) trans-Cinnamaldehyde and (B) poly(α -isopropylhydrocinnamyl alcohol) in CDCl₃. (C) FT-IR spectrum of poly(α -isopropylhydrocinnamyl alcohol). (D) polymerization process traced by ¹H NMR spectra: 0h, 15min, 1h, 24h. (E) polymerization process traced by ¹³C NMR spectra. (F) GPC curve of poly(α -isopropylhydrocinnamyl alcohol) in DMF. (G) standard curve of GC. (H) cinnamaldehyde consumption kinetic analysis by GC at reaction times of 0, 5, 10, and 15 min. (I) the remaining amount of cinnamaldehyde at reaction times of 0, 5, 10, and 15 min.



Scheme S1 Plausible Mechanism of Barbier polymerization of cinnamaldehyde.



Fig. S4 (A) TGA curves of $poly(\alpha$ -isopropylhydrocinnamyl alcohol), (B) DSC curves of $poly(\alpha$ -isopropylhydrocinnamyl alcohol), and (C) ICP standard curve and 12 mg $poly(\alpha$ -isopropylhydrocinnamyl alcohol) test results.

Characterization of luminescent properties



Fig. S5 Electron cloud distributions and energy levels (eV) of α -isopropylhydrocinnamyl alcohol, dimer, trimer, and tetramer in the ground state calculated using the DFT B3LYP/6-31G, Gaussian 09 program.



Fig. S6 The formation of aggregates in the investigation of AIE properties. (A) FESEM image of poly(α -isopropylhydrocinnamyl alcohol) (0.5 mg/mL) in 90% water/ THF mixtures, (B) magnified FESEM image, and (C) DLS size distributions of poly(α -isopropylhydrocinnamyl alcohol) (0.5 mg/mL) in 90% water/ THF mixtures.

Artificial light-harvesting system experiments



Fig. S7 (A) Emission spectra of the artificial light-harvesting system using $poly(\alpha$ -isopropylhydrocinnamyl alcohol as an energy donor and NiR as an energy acceptor, (B) Emission intensities (at 610 nm) of the artificial light-harvesting system.

The detection of TNT



Fig. S8 TNT sensory application of $poly(\alpha$ -isopropylhydrocinnamyl alcohol. (A) Emission spectra and (B) intensities and quenching ratio of $poly(\alpha$ -isopropylhydrocinnamyl alcohol in 0.3 mg/mL 90% water/THF mixtures (vol%) upon addition of TNT, excitation wavelength = 470 nm, (C) Photographic images of $poly(\alpha$ -isopropylhydrocinnamyl alcohol formed in 0.3 mg/mL 90% water/THF mixtures (vol%) under irradiation with UV lamp @ 365 nm, before and after adding of 80 ppm amounts of TNT, respectively, (D) Photographic image of TNT test strips ((a): blank, (b): with residual TNT under irradiation with UV lamp @ 365 nm, respectively, (E) Natural transition orbitals of Tetramer, (F) Natural transition orbitals of Tetramer/TNT complexes.

Computational method

Geometrical optimizations of tetramer and tetramer/TNT complex in ground state were calculated by density functional theory (DFT) at the level of theory B3LYP with the basis set 6-31G for all atoms. The vertical excited state of Tetramer and Tetramer/TNT complexes were calculated by time dependent density functional theory (TD-DFT) at the same level for geometrical optimization of ground state. Natural transition orbitals (NTOs) then were also calculated which can be helpful to generate the transition orbitals involved in the excited states and to give a qualitative description of electronic excitations. All calculations were performed by the Gaussian 09 package.

Coordinate of optimized structures

structure of Tetramer

6	-3.004397	-0.983775	-0.740744
6	-2.008464	0.027058	-0.142522
1	-2.892762	-1.927780	-0.249580
6	-0.571123	-0.488357	-0.342078
1	-2.203602	0.143847	0.903026
6	0.424645	0.522381	0.257130
1	-0.376142	-0.604075	-1.387732
1	0.310957	1.467574	-0.231326
6	-4.441561	-0.467899	-0.541034
1	-4.553152	0.476352	-1.031993
6	1.862315	0.009187	0.053005
1	1.976212	-0.936825	0.539898
6	2.858519	1.018205	0.653783
1	2.665918	1.129319	1.700414
6	4.296042	0.505023	0.447713
1	4.488445	0.393922	-0.599018
1	-5.133650	-1.170101	-0.956821
1	4.988293	1.206019	0.865258
6	-4.721845	-0.300491	0.963774
6	-4.445965	0.919158	1.596282
6	-5.252626	-1.367815	1.700614
6	-4.700757	1.071537	2.965800
1	-4.040711	1.734040	1.033502
6	-5.507367	-1.215519	3.070185
1	-5.463312	-2.299005	1.217518
6	-5.231425	0.004151	3.702792
1	-4.490104	2.002799	3.448754
1	-5.912478	-2.030423	3.632874
1	-5.425878	0.120493	4.748520
6	-2.168938	1.385435	-0.850115
6	-2.060840	1.465600	-2.245079
6	-2.422919	2.541155	-0.099473
6	-2.206433	2.701509	-2.889422
1	-1.867045	0.583085	-2.818278
6	-2.568469	3.777125	-0.743788
1	-2.505603	2.479986	0.965585
6	-2.460322	3.857311	-2.138750
1	-2.123815	2.762689	-3.954585
1	-2.762259	4.659611	-0.170662
1	-2.571621	4.801029	-2.630602

6	0.146681	0.686237	1.763027
6	-0.381153	-0.383151	2.499127
6	0.421872	1.905212	2.397348
6	-0.632953	-0.233763	3.869666
1	-0.591919	-1.313661	2.014794
6	0.170093	2.054604	3.767839
1	0.824223	2.721942	1.835224
6	-0.357107	0.985047	4.504050
1	-1.035773	-1.050259	4.431711
1	0.380395	2.985318	4.252152
1	-0.549064	1.099032	5.550488
6	2.694698	2.380343	-0.045623
6	2.967317	3.563893	0.653443
6	2.273069	2.436408	-1.380928
6	2.818290	4.803585	0.017320
1	3.289258	3.520987	1.673027
6	2.124116	3.676171	-2.017161
1	2.064911	1.532672	-1.914667
6	2.396658	4.859756	-1.317989
1	3.026411	5.707192	0.551125
1	1.802283	3.719092	-3.036681
1	2.282836	5.806358	-1.803710
6	-2.724162	-1.151776	-2.245528
1	-1.725714	-1.510481	-2.384688
6	-3.720793	-2.162216	-2.842961
1	-3.526716	-2.279029	-3.888730
6	-3.560016	-3.520932	-2.136076
1	-2.561715	-3.879757	-2.275849
1	-3.753903	-3.404021	-1.090321
1	-4.252664	-4.223063	-2.550977
6	-5.157676	-1.645667	-2.642057
1	-5.269291	-0.701680	-3.133358
1	-5.850343	-2.347777	-3.056914
1	-5.351752	-1.528557	-1.596278
8	-2.873285	0.109866	-2.902023
1	-2.698984	0.004998	-3.840235
6	-0.410073	-1.847660	0.363942
1	-0.605699	-1.731835	1.409516
6	1.027475	-2.362792	0.164842
1	1.606255	-1.618388	-0.340865

6	0.999159	-3.651119	-0.678334
1	1.998002	-4.008849	-0.816720
1	0.420492	-4.395689	-0.172715
1	0.559248	-3.443915	-1.631484
6	1.660440	-2.660833	1.536822
1	1.081645	-3.405313	2.042562
1	2.659319	-3.018600	1.398531
1	1.680069	-1.765657	2.122569
8	-1.334083	-2.786363	-0.192671
1	-1.233734	-3.633524	0.247637
6	2.139812	-0.151192	-1.453282
1	2.024745	0.794889	-1.939672
6	3.577758	-0.662317	-1.659363
1	4.269148	0.039925	-1.242484
6	3.854013	-0.822328	-3.165833
1	4.853084	-1.177392	-3.309475
1	3.162552	-1.524443	-3.582602
1	3.738335	0.123695	-3.652106
6	3.744393	-2.023746	-0.959295
1	3.053102	-2.726088	-1.376092
1	4.743567	-2.378636	-1.102845
1	3.552358	-1.912476	0.087456
8	1.215798	-1.089409	-2.010893
1	1.388613	-1.189303	-2.949946
6	4.460247	-0.857168	1.147034
1	4.644995	-0.702707	2.189607
6	5.646082	-1.615875	0.522428
1	5.461360	-1.770322	-0.520187
6	6.934410	-0.790612	0.698709
1	7.119083	-0.635897	1.741253
1	7.758114	-1.318286	0.265042
1	6.821186	0.155631	0.212306
6	5.809366	-2.977976	1.222117
1	5.994220	-2.823595	2.264681
1	4.914267	-3.551417	1.099674
1	6.633049	-3.505313	0.788141
8	3.264657	-1.624281	0.983130
1	3.367239	-2.473540	1.418864

structure of Tetramer/TNT complexes

6	-0.903063	-1.456998	-0.921692
6	-0.082157	-0.361853	-0.215785
1	-0.662026	-2.410628	-0.500575
6	1.419939	-0.642256	-0.406858
1	-0.314546	-0.359420	0.828666
6	2.240676	0.452692	0.300019
1	1.652015	-0.643648	-1.451338
1	1.997374	1.406974	-0.118376
6	-2.405056	-1.176127	-0.730425
1	-2.646090	-0.222264	-1.151318
6	3.742860	0.174893	0.104573
1	3.986523	-0.780039	0.521355
6	4.564252	1.268084	0.812899
1	4.335195	1.265209	1.858079
6	6.066330	0.990432	0.615510
1	6.295192	0.993298	-0.429776
1	-2.975550	-1.936916	-1.221025
1	6.637129	1.749915	1.107776
6	-2.738859	-1.173213	0.772771
6	-2.661682	0.018991	1.505174
6	-3.119639	-2.362756	1.408254
6	-2.965188	0.021708	2.873237
1	-2.370947	0.927204	1.019781
6	-3.423083	-2.360117	2.776364
1	-3.178612	-3.272984	0.848887
6	-3.345850	-1.167892	3.508869
1	-2.906255	0.932014	3.432466
1	-3.713672	-3.268323	3.261670
1	-3.577500	-1.165813	4.553488
6	-0.428817	1.010465	-0.822576
6	-0.304531	1.217437	-2.203066
6	-0.868375	2.052124	0.005310
6	-0.619519	2.466136	-2.755679
1	0.030973	0.421999	-2.835253
6	-1.183329	3.300887	-0.547270
1	-0.963423	1.894116	1.059314
6	-1.058998	3.507886	-1.927755
1	-0.524535	2.624154	-3.809790
1	-1.518823	4.096303	0.084843
1	-1.299646	4.461339	-2.349568

6	1.909673	0.452358	1.804106
6	1.532130	-0.738726	2.438789
6	1.986231	1.643651	2.538242
6	1.232007	-0.738599	3.807739
1	1.473002	-1.648197	1.878240
6	1.686129	1.643788	3.907145
1	2.273807	2.553205	2.053547
6	1.309236	0.452622	4.541947
1	0.943935	-1.647985	4.292357
1	1.744769	2.553394	4.467674
1	1.080391	0.452688	5.587175
6	4.213547	2.642960	0.214443
6	4.291491	3.793751	1.010314
6	3.816514	2.743366	-1.125795
6	3.972371	5.045013	0.466068
1	4.594666	3.716989	2.033657
6	3.497459	3.994719	-1.670142
1	3.757005	1.864642	-1.733452
6	3.575319	5.145523	-0.874165
1	4.031862	5.923600	1.073779
1	3.194387	4.071506	-2.693417
1	3.331617	6.100956	-1.289733
6	-0.569221	-1.460506	-2.424911
1	0.474321	-1.655907	-2.558227
6	-1.390893	-2.555429	-3.130025
1	-1.159543	-2.558025	-4.174733
6	-1.043866	-3.927981	-2.523956
1	-0.000439	-4.123473	-2.657897
1	-1.275042	-3.925260	-1.479247
1	-1.614943	-4.688854	-3.013686
6	-2.892732	-2.273949	-2.937507
1	-3.133744	-1.320323	-3.358761
1	-3.463832	-3.034807	-3.427193
1	-3.124125	-2.271062	-1.892766
8	-0.891285	-0.185983	-2.987787
1	-0.683537	-0.188352	-3.925047
6	1.767341	-2.015277	0.198314
1	1.534612	-2.013868	1.242702
6	3.269588	-2.295407	0.007724
1	3.741190	-1.435701	-0.420483

6	3.451842	-3.501937	-0.931744
1	4.495612	-3.696382	-1.064203
1	2.980379	-4.361784	-0.503634
1	3.006101	-3.285915	-1.880216
6	3.910916	-2.606181	1.372978
1	3.439311	-3.465968	1.801212
1	4.954725	-2.800665	1.240613
1	3.784237	-1.767837	2.025632
8	1.005881	-3.032062	-0.458269
1	1.222364	-3.887799	-0.080814
6	4.072890	0.178617	-1.399651
1	3.828049	1.133406	-1.815966
6	5.575080	-0.096943	-1.596879
1	6.144855	0.663695	-1.105211
6	5.903830	-0.093025	-3.101300
1	6.947538	-0.284386	-3.238785
1	5.333964	-0.853558	-3.592852
1	5.658392	0.861607	-3.517522
6	5.928445	-1.470759	-0.997619
1	5.358782	-2.231488	-1.489210
1	6.972228	-1.661941	-1.134996
1	5.699923	-1.473407	0.047712
8	3.311374	-0.837611	-2.057192
1	3.516928	-0.835228	-2.994958
6	6.417425	-0.384432	1.213889
1	6.555006	-0.288676	2.270701
6	7.716199	-0.907588	0.572432
1	7.578641	-1.003323	-0.484420
6	8.862771	0.081563	0.853283
1	9.000241	0.177562	1.910082
1	9.765019	-0.282498	0.407860
1	8.619728	1.036784	0.437029
6	8.066361	-2.282528	1.171154
1	8.204060	-2.186834	2.227954
1	7.269761	-2.969837	0.976053
1	8.968545	-2.646236	0.725448
8	5.353580	-1.303594	0.952848
1	5.572682	-2.160703	1.325657
6	-6.237512	-1.163921	0.064747
6	-6.424767	-0.605048	1.329290

6	-6.536263	0.777944	1.471146
6	-6.459323	1.602825	0.348262
6	-6.271638	1.044048	-0.915890
6	-6.161114	-0.339453	-1.057735
1	-6.150077	-2.254345	-0.046931
1	-6.684488	1.218483	2.467766
7	-5.963580	-0.928064	-2.390182
8	-5.902090	-0.192267	-3.335296
8	-5.871797	-2.120585	-2.478950
7	-6.506256	-1.474383	2.511878
8	-6.667613	-0.963776	3.585034
8	-6.408130	-2.659534	2.356324
7	-6.576796	3.060441	0.498115
8	-6.506570	3.742429	-0.485948
8	-6.738173	3.509457	1.598456
6	-6.186659	1.954017	-2.155380
1	-7.165990	2.093536	-2.563234
1	-5.778930	2.902499	-1.874239
1	-5.556011	1.498267	-2.889870