Electronic Supplementary Information

Mechano-, thermo-, solvato-, and vapochromism in bis(acetato-κ¹O)[4'-(4-(diphenylamino)phenyl)-](2,2':6',2"-terpyridine-κ³*N*,*N*',*N*")zinc(II) and its polymer

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Methods

Materials. Ligand **L1**[S1] and complex **C1**[S2] were synthesized according to previous reports. Single crystals of **C1·MeOH**, and powdery polycrystals of **C1** were prepared according to the previous report.[S2] Diethyl ether, methanol, benzyl alcohol, triethylamine and zinc carbonate were purchased from Kanto Chemical Co., Inc. *i*-Butanol and *s*-butanol were supplied by Nacalai Tesque, Inc. *n*-Butanol, *t*-butanol, *n*-propanol, ethanol and PAA (mean molecular weight = 1,000,000) were purchased from Wako Pure Chemical Industries, Ltd. Dichloromethane were supplied by Asahi Glass Co., Ltd. All solvents were used as received.

Preparation of C1-PAA. 1.6 mg of **L1** (3.4 μmol) and 38 mg of PAA (0.53 unit mmol) were added to MeOH (10 mL), and the reaction mixture was sonicated for 10 min. Then 13 mg of $ZnCO_3$ (0.10 mmol) in MeOH (10mL) was added and sonicated for 10 min. The reaction mixture was evaporated under a reduced pressure, and a mixture of MeOH and CH_2Cl_2 (1:49 v/v) was added to produce orange yellow gummy solid of **C1-PAA**. After removal of the solvent under a reduced pressure, orange yellow solid of **C1-PAA** as a xerogel was obtained (38.7 mg).

Instruments. UV/vis absorption spectra were obtained on a JASCO V-570 spectrometer. Steady-state PL and excitation spectra were recorded on a HITACHI F-4500 or a JASCO FP-8600 spectrometer. Absolute fluorescence quantum yields were measured on Hamamatsu Photonics C9920-02G. Fluorescence lifetime measurements were conducted using Hamamatsu Photonics Quantaurus-Tau C11367-02. IR spectra as KBr pellets were recorded using a Thermo Scientific FT-IR iS50 spectrometer. A solid sample was placed into a mortar and ground together with KBr crystals. The resultant fine powder was pelletized by applying a pressure, which was subjected to FT-IR measurement.

Solid sample preparations for optical properties. For PL spectroscopy, complexes in the crystalline solid state were held gently between quartz substrates. For mechanochromism, single crystal of **C1·MeOH** was ground using a spatula on a glass substrate. For vapoluminochromism, crystal-solvent-free **C1** in a 6 mL vial was placed in a 50 mL vial poured with 5 mL solvent, then the bigger vial was closed. All measurements were carried out at room temperature under air otherwise stated.

DFT calculation methods. The gas phase structure of complex **C1** was optimized at the B3LYP /6-31+G* level of theory using the crystal structure of crystal-solvent-free **C1** as the initial geometry (Fig. S2). For the estimation of the ICT transition energy in the crystal phase, the molecular structures of **C1** and **C1·MeOH** were taken from the data of X-ray crystallographic analyses. The excitation energies of 10 low-lying excited states (S1–S10) were calculated using the TD-B3LYP/6-31+G* method in the gas phase. All calculations were performed by Gaussian 09 revision C.01.[S7] The calculated frontier molecular orbitals were plotted using a GaussView 5.0 program package with an isovalue of 0.02 atomic unit. Therein, the positive and negative wavefunctions were in brown and green, respectively.

Solvatochromism of C1-PAA gel. The gel was immersed into a plenty volume of organic solvent till reaching saturation of solvent uptake. The gel could mix with water at any mixing ratio, such that 0.2 mL of water was added to 1.5 mg of **C1-PAA**.
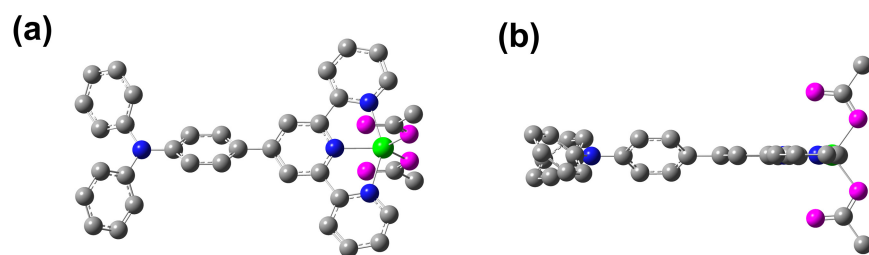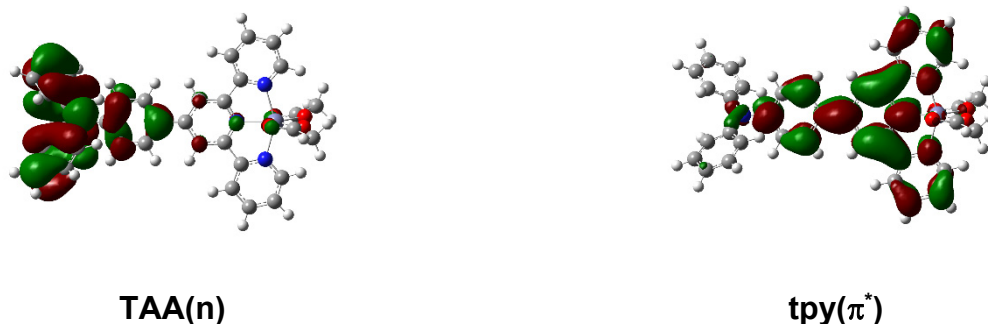
Fig. S1. DFT optimized structure of **C1** in the gas phase. (a) Oblique view; (b) Side view. The dihedral angle determined by the central pyridine and neighboring phenylene is 37.28°.

(a) C1

TAA(n)   **tpy(π*)**

(b) C1·MeOH

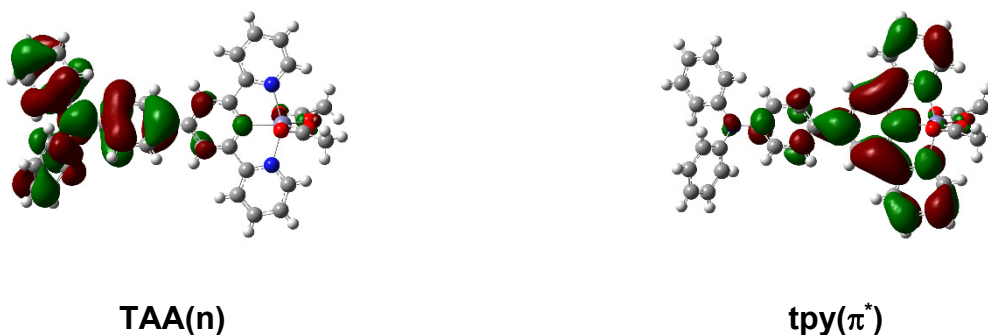**TAA(n)**   **tpy(π*)**

Fig. S2. Contour plots for frontier orbitals involved in the ICT transition provided by DFT/B3LYP/6-31+G*. (a) Isolate molecules from crystal lattices **C1**. (b) From crystal lattice **C1·MeOH**.

Table S1. Parameters of the ICT transition provided by TDDFT/B3LYP/6-31+G*.

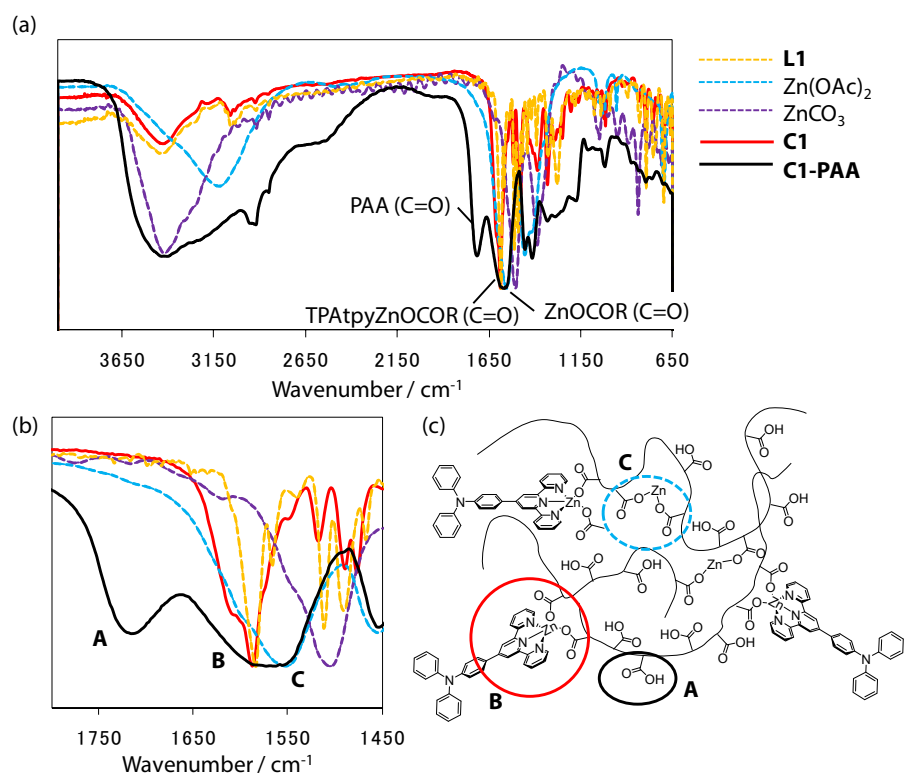| Complex	Transition energy / eV	Transition energy /nm	Oscillator strength	Occupancy / %
C1	2.6266	472.03	0.3226	93
C1·MeOH	2.8650	432.74	0.3829	98

Fig. S3. (a,b) IR spectra of **C1-PAA**, **C1**, **L1**, Zn(OAc)$_2$, and ZnCO$_3$. (a) whole region; (b) focusing on the C=O stretch region. (c) Plausible schematic illustration of the chemical structure of **C1-PAA**. A, B, C denote the residues that show the peaks labeled in (b).
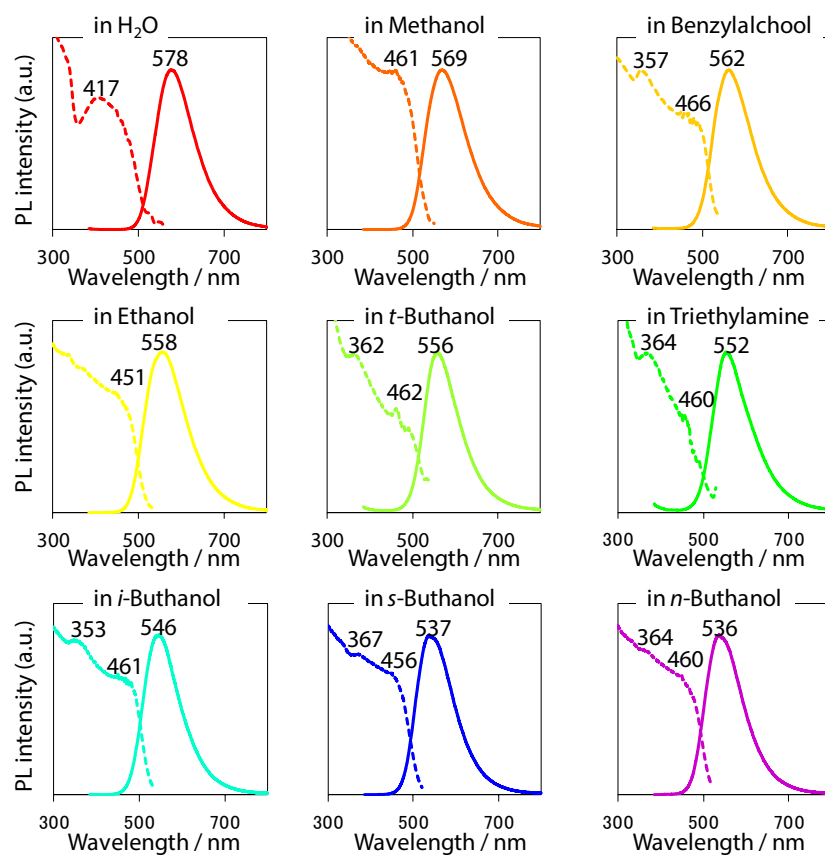
Fig. S4. Excitation and PL spectra of organo- and hydrogels of **C1-PAA**.

Table S2. Photophysical properties of organo- and hydrogels of **C1-PAA**

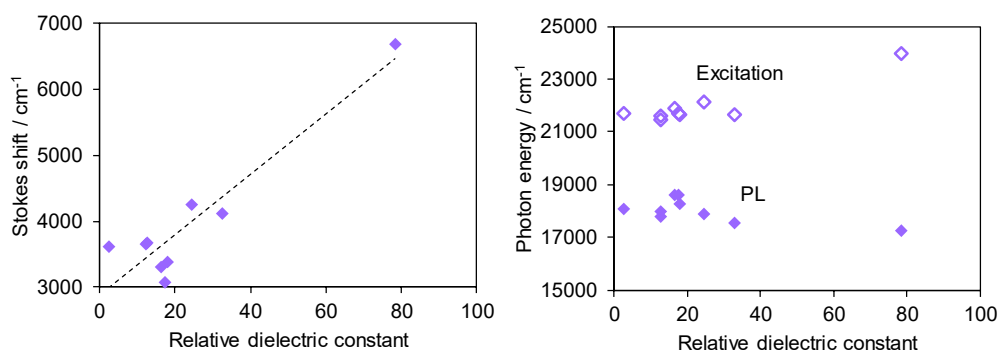|	Excitation photon energy		PL photon energy	
	nm	cm^{-1}	nm	cm^{-1}
n-BuOH	460	21700	536	18700
s-BuOH	456	21900	537	18600
i-BuOH	461	21700	546	18300
NEt$_3$	460	21700	552	18100
t-BuOH	462	21600	556	18000
EtOH	451	22200	558	17900
BzOH	466	21500	562	17800
MeOH	461	21700	569	17600
H$_2$O	417	24000	578	17300

Figure S5. (a) Plots between the Stokes shift of organo- and hydrogels of **C1-PAA** and relative dielectric constant. (b) Plots between the excitation or PL maximum of organo- and hydrogels of **C1-PAA** and relative dielectric constant.

References for Electronic Supplementary Information

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[S7] Gaussian 09 revision C.01, M. J. Frisch et al. Gaussian, Inc., Wallingford CT, 2009.