Electronic Supplementary Information

Co-Assemblies of Polydiacetylenes and Metal Ions for Solvent Sensing

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1. Calculations of the solubility parameters of the solvents

Table S1. Hansen parameters of THF, acetone, 1,4-dioxane and water

	δ_d/ $MPa^{1/2}$	δ_p/ $MPa^{1/2}$	δ_h/ $MPa^{1/2}$
THF	16.8	5.7	8.0
acetone	15.5	10.4	7
1,4-dioxane	19	1.8	7.4
Water	15.5	16.0	42.3

These data are taken from reference [1].

The Hansen parameters of the water/organic solvent mixtures can be estimated from the following equation: [1]

$$\delta_{average} = \Sigma\phi_i\delta_i \quad (1)$$

where $\delta_{average}$ is the average solubility parameter of the mixture, ϕ_i and δ_i are the volume fraction and solubility parameter of the component.

The Teas parameters of the water/organic solvent mixtures can be estimated from the following equations: [1-5]

$$f_d=\delta_d/(\delta_d + \delta_p + \delta_h) \quad (2)$$

$$f_p=\delta_p/(\delta_d + \delta_p + \delta_h) \quad (3)$$

$$f_h=\delta_h/(\delta_d + \delta_p + \delta_h) \quad (4)$$

where f_d is the dispersion component of Teas parameter, f_p is the polar component of Teas parameter, and f_h is the hydrogen bonding component of Teas parameter.

2. Calculations on the solubility parameters of the side chains and repeating unit of the backbone of PTDA

The Hansen parameters of side chains of PTDA and repeating unit of backbone of PTDA are calculated according to a group-contribution method reported in the literature. [5]

2.1. Calculations on the solubility parameters of the side chain of PTDA

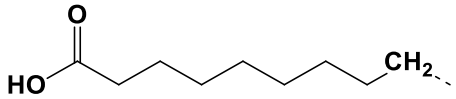

Figure S1. Chemical structure of the side chain of PTDA.

Table S2. 1st-Order group approximation for the prediction of the dispersion partial solubility parameter, δ_d, for the side chain of PTDA.

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
$-CH_2$	8	-0.0269	-0.2152
COOH	1	-0.2910	-0.2910
Constant, C			17.3231
$\Sigma N_i C_i + C$			15.8455

$\delta_d = 15.8455$

Table S3. 1st-Order group approximation for the prediction of the polar partial solubility parameter, δ_p, for the side chain of PTDA.

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
$-CH_2$	8	-0.3045	-2.436
COOH	1	0.9042	0.9042
Constant, C			7.3548
$\Sigma N_i C_i + C$			4.0168

Table S4. 2nd-Order group approximation for the prediction of the polar partial solubility parameter, δ_p, for the side chain of PTDA.

2nd -Order groups	Occurrences, M_j	Contributions, D_j	$M_j D_j$
CCOOH	1	-0.2187	-0.2187
$\Sigma M_j D_j$			-0.2187

$\delta_p = 4.0168 - 0.2187 = 3.7981$

Table S5. 1st-Order group approximation for the prediction of the hydrogen bonding partial solubility parameter, δ_h, for the side chain of PTDA.

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
$-CH_2$	8	-0.4119	-3.2952
COOH	1	3.791	3.791
Constant, C			7.7993
$\Sigma N_i C_i + C$			7.5138

Table S6. 2nd-Order group approximation for the prediction of the hydrogen bonding partial solubility parameter, δ_h, for the side chain of PTDA.

2nd -Order groups	Occurrences, M_j	Contributions, D_j	$M_j D_j$
CCOOH	1	1.1460	1.1460
$\Sigma M_j D_j$			1.1460

$\delta_h = 7.5138 + 1.1460 = 8.6598$

The Teas parameter of the side chain of PTDA can be calculated as follows:

$f_d = 15.8455 / (15.8455 + 3.7981 + 8.6598) = 0.56$

$f_p = 3.7981 / (15.8455 + 3.7981 + 8.6598) = 0.13$

$f_p = 8.6598/ (15.8455 + 3.7981 + 8.6598) = 0.31$

2.2. Calculations on the solubility parameters of the alkyl chain of PTDA

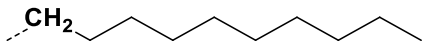

Figure S2. Chemical structure of the alkyl side chain.

Table S7. 1st-Order group approximation for the prediction of the dispersion partial solubility parameter, δ_d, for the alkyl chain

1^{st}-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
$-CH_3$	1	-0.9714	-0.9714
$-CH_2$	9	-0.0269	-0.2421
Constant, C			17.3231
$\Sigma N_i C_i + C$			16.1096

$\delta_d = 16.1096$

Table S8. 1^{st}-Order group approximation for the prediction of the polar partial solubility parameter, δ_p, for the alkyl chain

1^{st}-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
$-CH_3$	1	-1.6448	-1.6448
$-CH_2$	9	-0.3045	-2.7405
Constant, C			7.3548
$\Sigma N_i C_i + C$			2.9695

$\delta_p = 2.9695$

Table S9. 1^{st}-Order group approximation for the prediction of the hydrogen bonding partial solubility parameter, δ_h, for the alkyl chain

1^{st}-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
$-CH_3$	1	-0.7813	-0.7813
$-CH_2$	9	-0.4119	-3.7071
Constant, C			7.7993
$\Sigma N_i C_i + C$			3.3109

$\delta_h = 3.3109$

The Teas parameter of the alkyl chain can be calculated as follows:

$f_d = 16.10965 / (16.1096 + 2.9695 + 3.3109) = 0.72$

$f_p = 2.9695 / (16.1096 + 2.9695 + 3.3109) = 0.13$

$f_p = 3.3109 / (16.1096 + 2.9695 + 3.3109) = 0.15$

2.3. Calculations on the solubility parameters of the repeating unit of backbone of PTDA

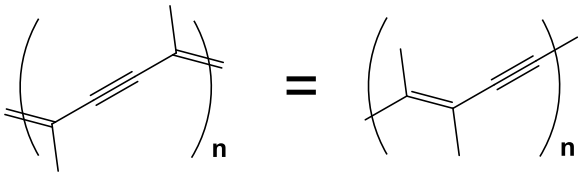

Figure S3. Chemical structure of the conjugated backbone of PTDA.

Table S10. 1st-Order group approximation for the prediction of the dispersion partial solubility parameter, δ_d, for the repeating unit of conjugated backbone of PTDA

1st-Order groups	Occurrences, N_i	Contributions, C_i	N_i C_i
-CH_3	1	-0.9714	-0.9714
>C=C<	1	0.3592	0.3592
C≡C	1	-0.2028	-0.2028
Constant, C			17.3231
$\Sigma N_i C_i$ +C			16.5081

Table S11. 2nd-Order group approximation for the prediction of the dispersion partial solubility parameter, δ_d, for the repeating unit of conjugated backbone of PTDA

2nd -Order groups	Occurrences, M_j	Contributions, D_j	M_j D_j
>C-C=	2	-0.2798	-0.5596
$\Sigma M_j D_j$			-0.5596

δ_d = 16.5081-0.5596 = 15.9485

Table S12. 1st-Order group approximation for the prediction of the polar partial solubility parameter, δ_p, for the repeating unit of conjugated backbone of PTDA

1st-Order groups	Occurrences, N_i	Contributions, C_i	N_i C_i
-CH_3	1	-1.6448	-1.6448
>C=C<	1	1.0526	1.0526
C≡C	1	-0.7598	-0.7598
Constant, C			7.3548
$\Sigma N_i C_i$ +C			6.0028

δ_p = 6.0028

Table S13. 1st-Order group approximation for the prediction of the hydrogen bonding partial solubility parameter, δ_h, for the repeating unit of conjugated backbone of PTDA

1st-Order groups	Occurrences, N_i	Contributions, C_i	$N_i C_i$
$-CH_3$	1	0.29901	0.29901
>C=C<	1	-0.12117	-0.12117
C≡C	1	-0.35107	-0.35107
Constant, C			1.3720
$\Sigma N_i C_i$ +C			1.19877

Table S14. 2nd-Order group approximation for the prediction of the hydrogen bonding partial solubility parameter, δ_h, for the repeating unit of conjugated backbone of PTDA

2nd -Order groups	Occurrences, M_j	Contributions, D_j	$M_j D_j$
>C-C=	2	0.342229	0.684458
$\Sigma M_j D_j$			0.684458

δ_h = 1.19877 + 0.684458 = 1.883228

The Teas parameter of the repeating unit of PTDA can be calculated as follows:

f_d = 15.9485 / (15.9485 + 6.0028 + 1.883228) = 0.67

f_p = 6.0028 / (15.9485 + 6.0028 + 1.883228) = 0.25

f_p = 1.883228 / (15.9485 + 6.0028 + 1.883228) = 0.08

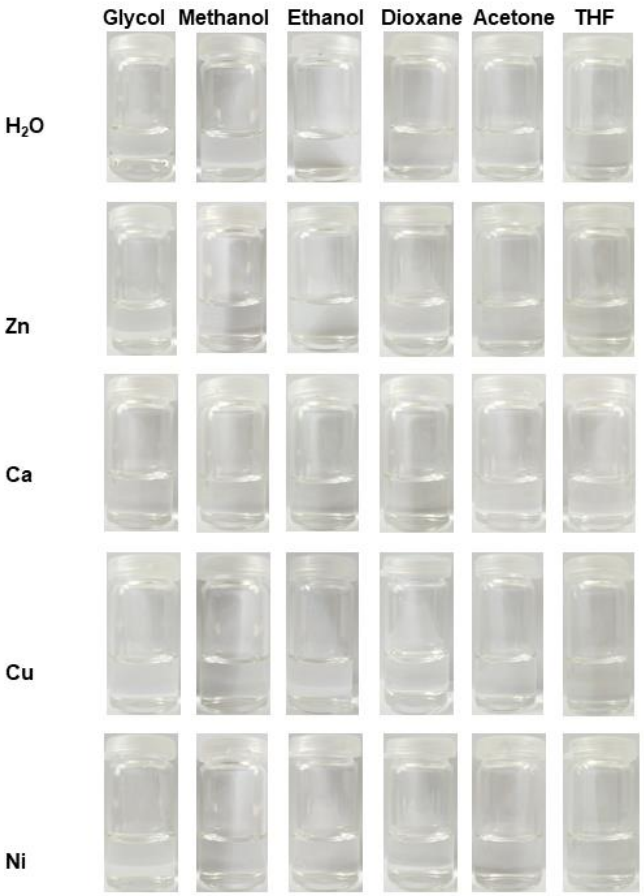

Figure S4. Photographs of water and aqueous solutions of $M(NO_3)_2$ (M = Zn, Cu, Ca, Ni) after exposure to organic solvents. The volume fractions of the solvents are 33.3%. This is a control experiment for Figure 9 in the main manuscript.

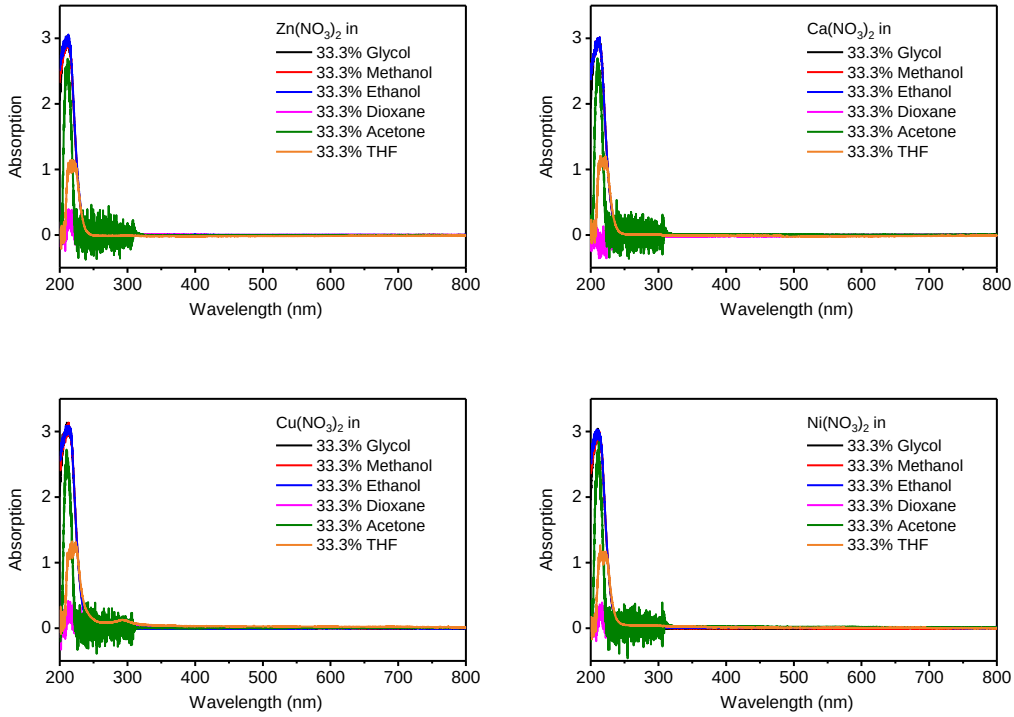

Figure S5. UV-vis absorption of $M(NO_3)_2$ (M = Zn, Cu, Ca, Ni) in aqueous solutions with 33.3% organic solvents such as glycol, methanol, ethanol, dioxane, acetone, and THF. The photographs of the solutions are in Figure S4. This is a control experiment for Figure 9 in the main manuscript.

References

[1] Barton AFM. Solubility parameters. Chem Rev 1975; 75: 731-753.

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