Table S1. Comparison between the lattice parameters of 3,3′-diaminobenzidine optimized by different force fields and the experimental values

	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*RAD* (%)
Experimental	9.639	7.471	7.754	90.000	95.690	90.000	0
COMPASS	9.513	7.195	7.850	90.000	96.600	90.000	1.2
COMPASS II	9.513	7.195	7.850	90.000	96.600	90.000	1.2
Universal	11.190	6.903	7.313	90.000	92.692	90.000	5.4
cvff	7.317	8.029	8.978	90.000	85.636	90.000	9.6
Dreiding	7.585	6.828	10.118	90.000	96.818	90.000	10.3

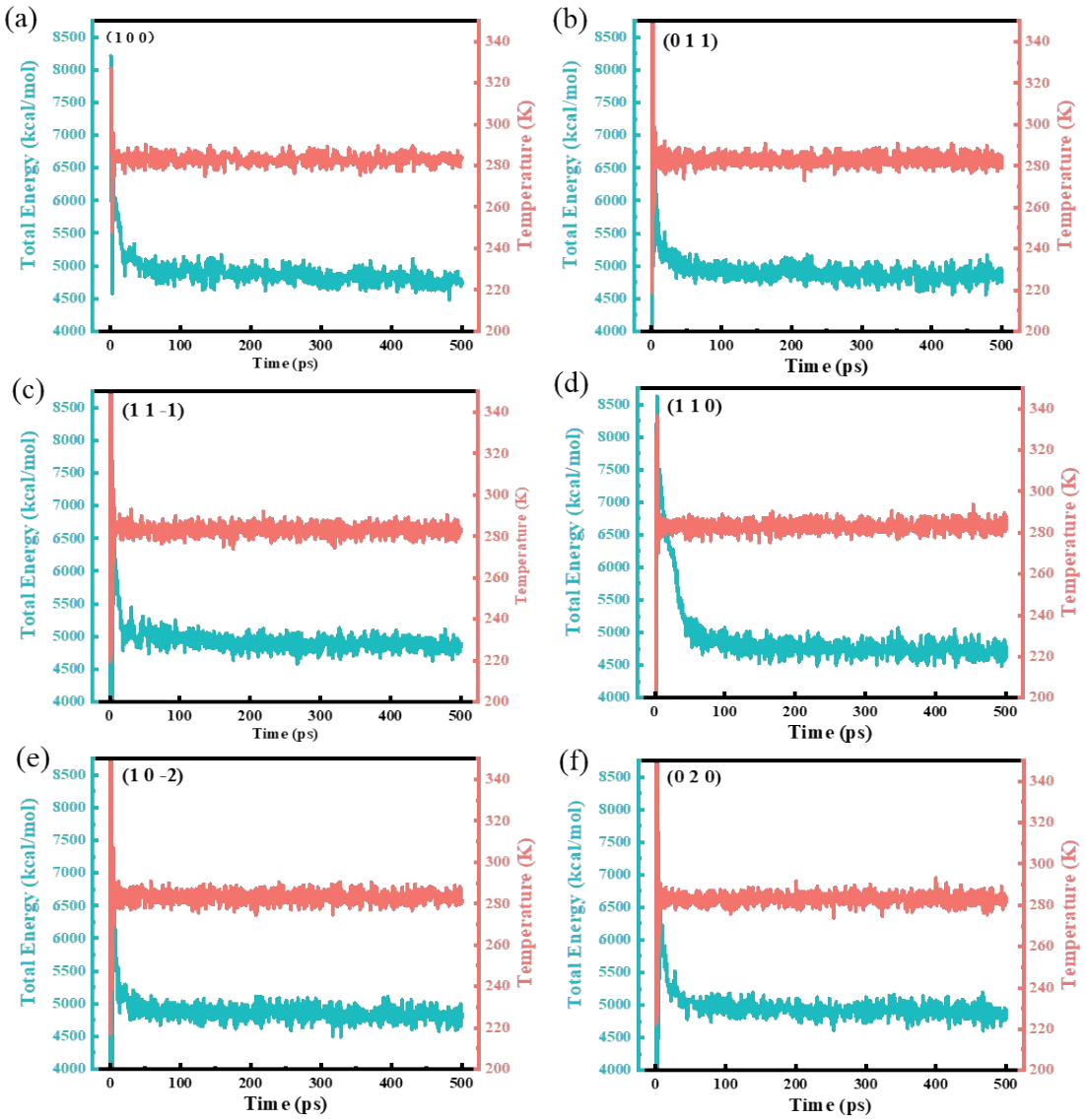

Figure S1. Total energy and temperature changes in each double-layer model box during molecular dynamics simulation

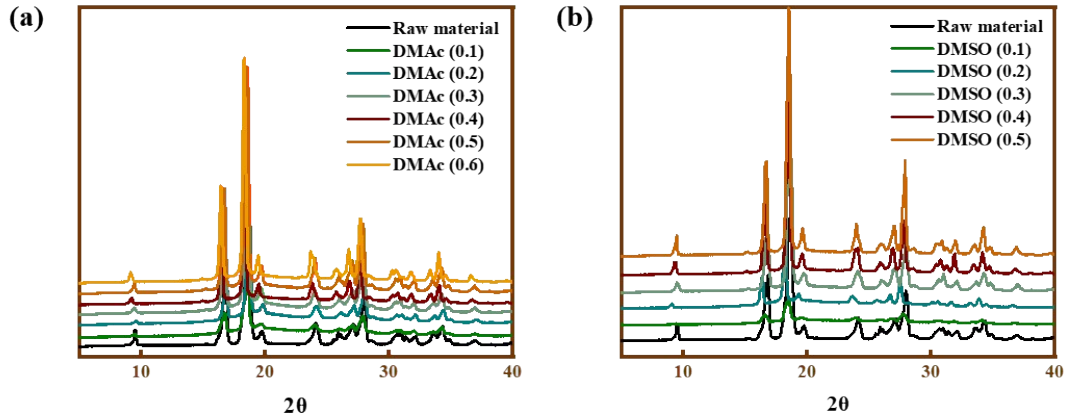

Figure S2. PXRD pattern of samples after drying with saturated solution of 3,3′-diaminobenzidine in binary mixed solvents (a)DMAc + water, (b)DMSO + water

Table S2. Experimental and calculated molar solubility of 3,3′-diaminobenzidine at different temperatures in a binary mixture of DMAc and water

T(K)	$10^3 x^{exp}$	$10^3 x^{cal}$
	x_{DMAc}=0.1	
278.15	0.9420	0.9457
283.15	1.0307	1.0807
288.15	1.1722	1.2628
293.15	1.4011	1.5063
298.15	1.9602	1.8315
303.15	2.5504	2.2668
308.15	2.9479	2.8523
313.15	3.4893	3.6446
318.15	4.5507	4.7240
323.15	6.2296	6.2048
328.15	8.3013	8.2510
	x_{DMAc}=0.2	
278.15	3.2015	3.2782
283.15	4.1496	3.9720
288.15	4.3603	4.8210
293.15	5.9702	5.8604
298.15	7.5996	7.1333
303.15	8.8004	8.6923
308.15	10.59	10.6020
313.15	12.83	12.9412
318.15	14.59	15.8064
323.15	20.77	19.3155
328.15	23.17	23.6122

Continued Table S2

T(K)	10^3x^{exp}	10^3x^{cal}
	x_{DMAc}=0.3	
278.15	10.07	10.0821
283.15	11.57	11.5956
288.15	13.27	13.3640
293.15	15.23	15.4305
298.15	18.32	17.8460
303.15	20.95	20.6697
308.15	23.73	23.9708
313.15	27.66	27.8306
318.15	31.79	32.3435
323.15	38.39	37.6201
328.15	43.56	43.7893
	x_{DMAc}=0.4	
278.15	23.42	23.1453
283.15	25.05	25.0467
288.15	26.37	27.3123
293.15	30.07	29.9943
298.15	34.27	33.1561
303.15	37.12	36.8742
308.15	40.70	41.2404
313.15	45.38	46.3642
318.15	52.41	52.3766
323.15	60.80	59.4335
328.15	67.07	67.7208
	x_{DMAc}=0.5	
278.15	43.25	42.9975
283.15	44.29	45.3147
288.15	47.22	47.9790

Continued Table S2

T(K)	10^3x^{exp}	10^3x^{cal}
293.15	51.52	51.0188
298.15	56.09	54.4672
303.15	59.25	58.3630
308.15	63.65	62.7508
313.15	66.49	67.6815
318.15	70.85	73.2130
323.15	79.33	79.4106
328.15	87.62	86.3483
	x_{DMAc}=0.6	
278.15	65.36	64.8260
283.15	66.79	67.0865
288.15	68.40	69.7548
293.15	73.48	72.8479
298.15	76.77	76.3882
303.15	81.55	80.4036
308.15	84.13	84.9272
313.15	89.34	89.9977
318.15	96.27	95.6596
323.15	101.59	101.9636
328.15	109.14	108.9668

Table S3. Experimental and calculated molar solubility of 3,3′-diaminobenzidine at different temperatures in a binary mixture of DMSO and water

T(K)	$10^3 x^{exp}$	$10^3 x^{cal}$
	x_{DMSO}=0.1	
278.15	0.5035	0.5286
283.15	0.5897	0.6060
288.15	0.6680	0.7098
293.15	0.8122	0.8478
298.15	1.073	1.031
303.15	1.421	1.276
308.15	1.709	1.605
313.15	1.964	2.047
318.15	2.518	2.647
323.15	3.479	3.467
328.15	4.633	4.595
	x_{DMSO}=0.2	
278.15	1.949	2.106
283.15	2.453	2.495
288.15	3.062	2.987
293.15	3.664	3.609
298.15	4.618	4.397
303.15	5.461	5.401
308.15	6.623	6.683
313.15	8.171	8.324
318.15	10.27	10.43
323.15	13.36	13.15
328.15	16.63	16.67

Continued Table S3

T(K)	10^3x^{exp}	10^3x^{cal}
	x_{DMSO}=0.3	
278.15	8.912	9.141
283.15	10.23	10.53
288.15	11.95	12.15
293.15	14.35	14.04
298.15	17.16	16.25
303.15	19.27	18.83
308.15	21.79	21.84
313.15	23.92	25.35
318.15	29.78	29.46
323.15	34.32	34.25
328.15	39.98	39.84
	x_{DMSO}=0.4	
278.15	31.39	31.42
283.15	33.44	33.80
288.15	36.81	36.51
293.15	40.40	39.58
298.15	42.52	43.05
303.15	46.98	46.98
308.15	50.46	51.41
313.15	57.07	56.41
318.15	62.56	62.05
323.15	67.87	68.40
328.15	75.68	75.56
	x_{DMSO}=0.5	
278.15	64.07	63.64
283.15	65.79	66.66
288.15	70.39	70.02

Continued Table S3

T(K)	10^3x^{exp}	10^3x^{cal}
293.15	73.84	73.76
298.15	77.95	77.91
303.15	82.82	82.48
308.15	86.98	87.51
313.15	92.51	93.03
318.15	100.0	99.09
323.15	105.6	105.7
328.15	112.8	113.0

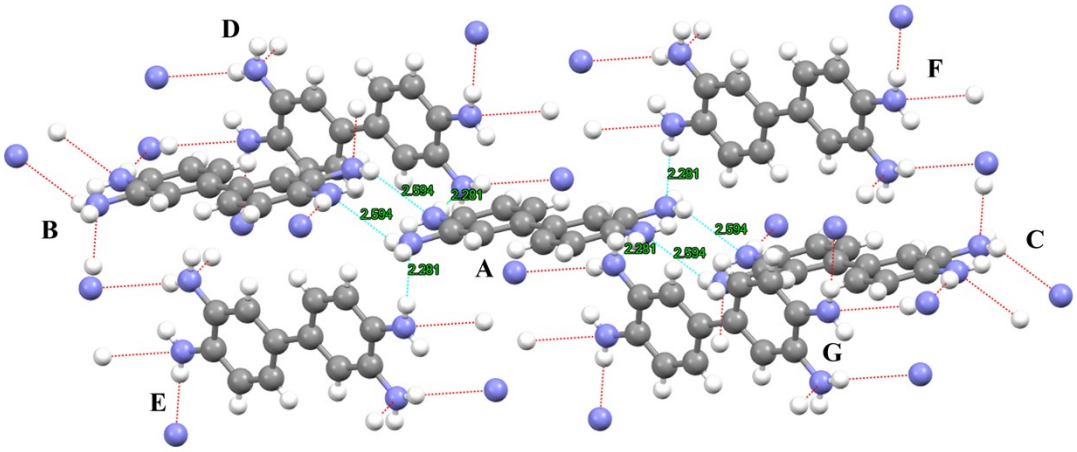

Figure S3. Intermolecular hydrogen bonds in crystals

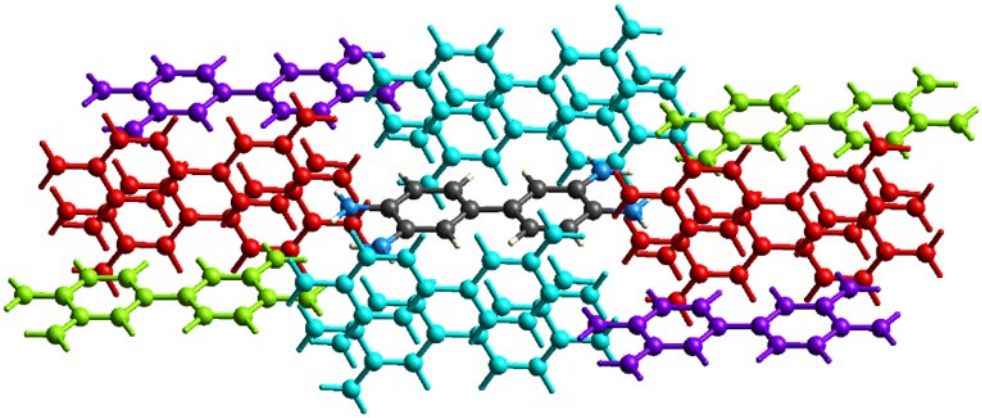

Figure S4. Calculation results of interaction energy between molecular pairs of 3,3′-diaminobenzidine

Table S4. Intermolecular interaction energy of 3,3′-diaminobenzidine crystals

color	R^a (Å)	E_{ele} (kcal·mol^{-1})	E_{pol} (kcal·mol^{-1})	E_{dis} (kcal·mol^{-1})	E_{rep} (kcal·mol^{-1})	$E_{tot}{}^b$ (kcal·mol^{-1})
	10.7	-4.3	-1.4	-4.7	8.2	-4.5
	11.7	-3.6	-1.2	-4.9	6.2	-5.1
	6					
	5.38	-3.2	-1.4	-9.6	6.4	-8.5
	9.64	-1.8	-0.5	-3.2	1.4	-4.1

R_a is the distance between molecular centroids.

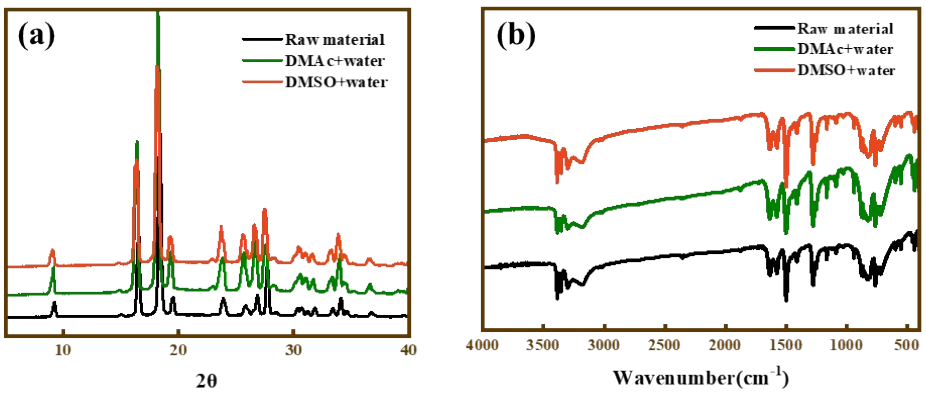

Figure S5. PXRD (a) and FTIR (b) patterns of 3,3′-diaminobenzidine prepared in different solvents

Table S5. Crystal habit parameters of 3,3'-diaminobenzidine in the presence of additive

Face	E_{int} (kcal·mol^{-1})	E_S (kcal·mol^{-1})	$E_{att'}$ (kcal·mol^{-1})	Relative growth rate	Area (%)
（1 0 0）	-541.04	-12.58	-30.94	2.90	14.72
（0 1 1）	-527.35	-13.71	-35.23	3.30	--
（1 1 -1）	-960.35	-38.59	-10.68	1.00	85.28
（1 1 0）	-533.41	-18.67	-38.66	3.62	--
（1 0 -2）	-498.92	-23.10	-43.05	4.03	--
（0 2 0）	-430.14	-8.44	-54.67	5.12	--