Bis-3,5-Diamino-1,2,4-Triazolyl-1,2,4,5-Tetrazine: From Insensitive High energy Density Materials to Small Molecule Organic Semiconductors

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SUPPORTING INFORMATION

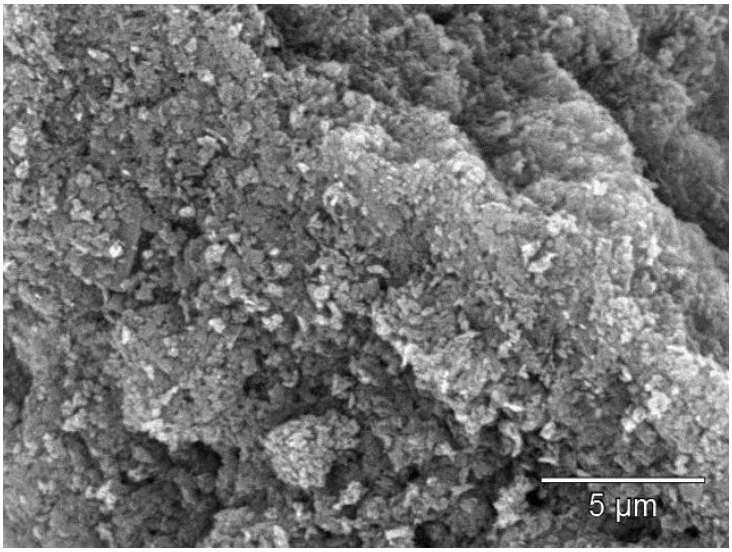


Figure S1. Scanning electron microscope (SEM) topographic image of IEF-12

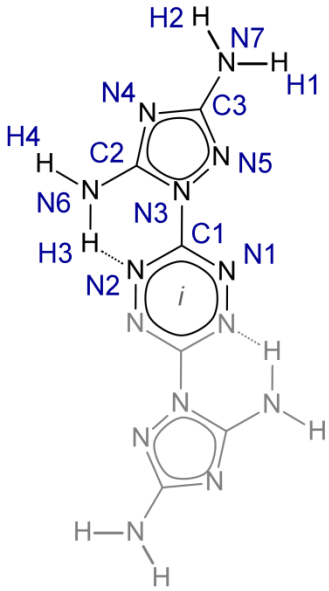
Table S1. Cartesian coordinates (Å units) of optimized *cis*-BDTT model

Atom	x	y	z
N2	1.491300	0.209217	0.258926
C3	0.763421	−0.930202	0.171699
N3	−0.572803	-0.974201	0.145685
N4	−1.221664	0.170801	0.127946
C6	−0.497451	1.295029	0.102867
N1	0.852112	1.339130	0.209564
N1’	−1.177126	2.492256	−0.009142
C5’	−2.491162	2.730656	−0.383549
N4’	−2.737242	4.019763	−0.361235
N2’	−0.561954	3.714747	0.273991
C3’	−1.538213	4.564103	0.036723
N1’’	1.445613	−2.129653	0.128107
N2’’	2.807764	−2.184497	−0.178926
C3’’	3.038406	−3.478277	−0.126996
C5’’	0.981163	−3.421980	0.327539
N4’’	1.963282	−4.280733	0.176745
N6’’	−0.286778	−3.719259	0.701369
N7’’	4.283026	−4.017598	−0.325546
N6’	−1.386192	5.921315	0.139817
N7’	−3.351434	1.761824	−0.787149
H1’’	4.941720	−3.421234	−0.803570
H2’’	4.286286	−4.981637	−0.622735
H3’’	−1.007141	−3.037546	0.508837
H4’’	−0.526674	−4.698064	0.700215
H1’	−0.583041	6.235406	0.662971
H2’	−2.235756	6.442466	0.290922
H3’	−3.178603	0.822969	−0.454371
H4’	−4.307311	2.062628	−0.900827

Table S2. Cartesian coordinates (Å units) of optimized *trans*-BDTT model

Atom	X	y	z
N2	4.678127	2.677032	8.518384
C3	5.124139	2.929118	7.272527
N3	6.013989	2.160014	6.617235
N4	6.561321	1.147594	7.240437
C6	6.172673	0.944289	8.512433
N1	5.224670	1.665269	9.140305
N1’	6.758350	−0.082816	9.228952
C5’	6.367765	−0.653427	10.433684
N4’	7.232563	−1.575126	10.793634
N2’	7.937563	−0.701244	8.800791
C3’	8.154984	−1.560453	9.774596
N1’’	4.618881	4.024018	6.600116
N2’’	3.569819	4.789145	7.120901
C3’’	3.401047	5.686664	6.172044
C5’’	4.976146	4.542705	5.359234
N4’’	4.217833	5.575956	5.072294
N6’’	5.997461	4.078420	4.607870
N7’’	2.501352	6.716088	6.267995
N6’	9.266294	−2.363289	9.830584
N7’	5.217215	−0.350227	11.080728
H1’’	1.773492	6.607287	6.957323
H2’’	2.214874	7.123048	5.391226
H3’’	6.372874	3.162659	4.811850
H4’’	6.094308	4.476875	3.687883
H1’	9.745175	−2.512077	8.955252
H2’	9.173107	−3.179803	10.414773
H3’	4.785906	0.542025	10.879852
H4’	5.120972	−0.744947	12.003095

For subsequent Rietveld refinement the model, as obtained from the structure solution, was symmetrized to match the array of atoms in the asymmetric unit cell to half of the molecule (Z' = 0.5) as it is shown on Scheme S1.



Scheme S1. Molecular diagram of *trans*-isomer. The asymmetric part of molecule (sketched with black color) is separated with dotted line, "i" symbol denotes the inversion center symmetry element.

Background contribution to the PXRD pattern was approximated with 36 Chebyshev polynomials. The peak profile was modeled in the full Voigt approximation (eqn 1-2):

$$f_G = p_1 \tan(\theta) + \frac{p_2}{\cos(\theta)} \text{ (eqn 1)}$$

$$f_L = p_3 \tan(\theta) + \frac{p_4}{\cos(\theta)} \text{ (eqn 2)}$$

where f_G, f_L are Gaussian and Lorentzian full width at a half of maximum and p_1-p_4 are adjustable parameters.

The reasonable values for the latter were obtained from NIST SRM 660c LaB_6 measured at the same conditions as the sample under study. The size parameters were refined isotropically and the microstrain was approximated by Stephens phenomenological model[1]. The aberrations of

MYTHEN 1D position sensitive detector were accounted using TOPAS macros published by Gozzo *et al.*[2] N1-N1' branch (Scheme S1) was restrained to be flat avoiding "fusing" of tetrazine cycle. We used statistically averaged (mean) values from Mogul report as the restraint parameters (C1–N1, C1–N3, C3–N5, C2–N3, C2–N6, C3–N7 and N4–C2–N3, C1–N1–N2, C1–N3–N5, N5–C3–N4, C2–N4–C3) for the additional PXRD refinements. Such a treatment was helpful to improve the model significantly against the CSD Mogul[3] check. Hydrogen atoms were placed upon convergence of the carbon/nitrogen crystal coordinates refinement. The positions of H-atoms were fixed to those were calculated with DFT+D(TS) approach and the isotropic displacement parameters were constrained as $B_{iso}(H) = 1.2 \times B_{iso}(N)$. The final plot of refined powder diffraction profile is depicted in Figure S2.

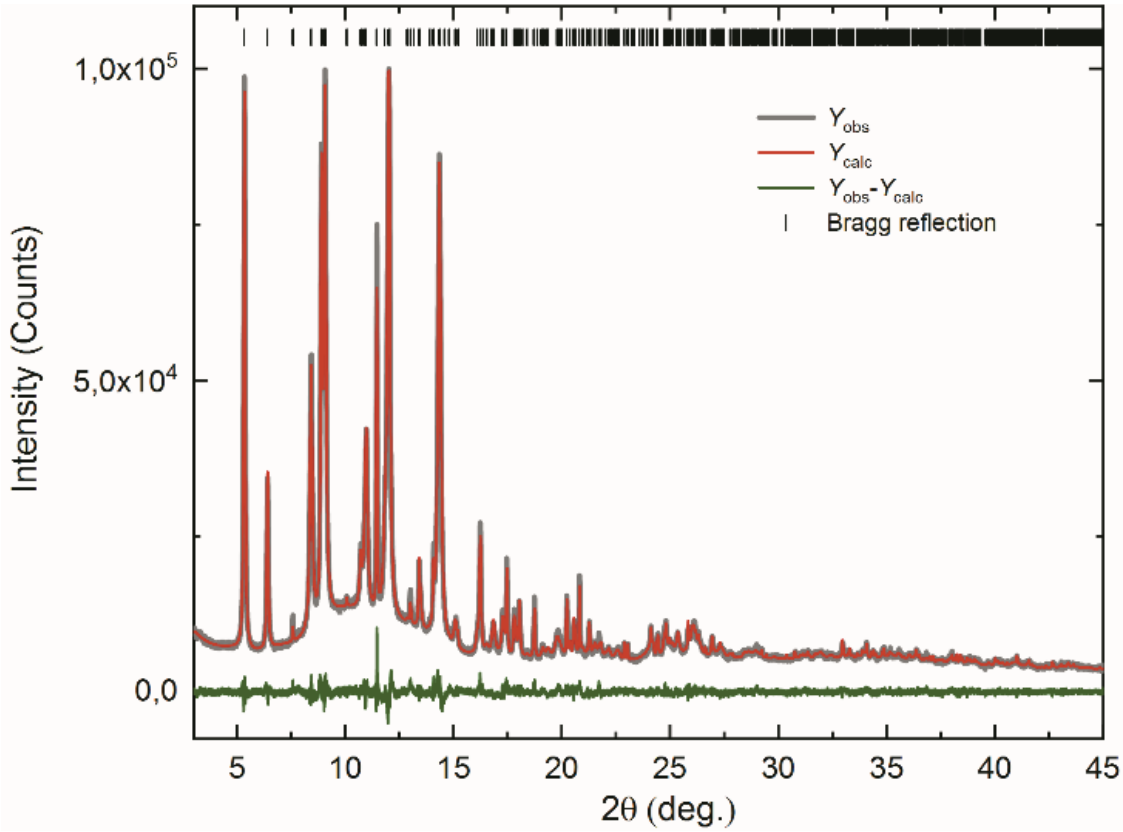


Figure S2. Plot of the Rietveld refinements of IEF-12 crystal structure (Rwp = 4.12%, Rp = 3.19%, GoF = 4.03 based on conventional Rietveld's definition, see ref. 4).

Table S3. Unit cell parameters, atomic coordinates and isotropic displacement parameters for the final model (the values obtained computationally are given in bold text).

Unit cell parameter (triclinic system, space group *P*-1)	
a, Å	5.27184(6)
	5.33020 (+1.1%)
b, Å	6.8523(1)
	6.8347 (-0.3%)
c, Å	8.07230(9)
	7.98353 (-1.1%)
α, °	97.0341(9)
	96.7845 (-0.3%)
β,°	100.684(1)
	99.684 (-1.0%)
γ, °	105.080(1)
	106.992 (-1.8%)
V, Å^3	272.190(6)
	269.832 (-0.9%)

Atom	*x*	*y*	*z*	B_{iso}
N1	0.35477(36)	0.11412(24)	0.56982(23)	2.351(30)
	0.34352	**0.10238**	**0.56963**	
C1	0.40429(38)	0.12022(26)	0.41440(22)	3.094(82)
	0.41499	**0.12378**	**0.41651**	
N2	0.57373(43)	0.02439(36)	0.35026(23)	$=B_{iso}$(N1)
	0.56769	**0.02523**	**0.34563**	
N3	0.33164(30)	0.26576(24)	0.32604(15)	$=B_{iso}$(N1)
	0.32577	**0.25809**	**0.32519**	
C2	0.38538(27)	0.32040(33)	0.17605(17)	$=B_{iso}$(C1)
	0.37225	**0.31097**	**0.16826**	
N4	0.26507(34)	0.46081(22)	0.13569(15)	$=B_{iso}$(N1)
	0.25821	**0.45435**	**0.13128**	
N5	0.17414(36)	0.37759(27)	0.38920(19)	$=B_{iso}$(N1)
	0.17648	**0.37334**	**0.39109**	

C3	0.13759(28)	0.48747(20)	0.26440(24)	$=B_{iso}$(N1)
	0.14458	**0.48818**	**0.27032**	
N6	0.50506(44)	0.22273(30)	0.07110(28)	$=B_{iso}$(N1)
	0.50520	**0.22723**	**0.06723**	
N7	0.03496(40)	0.65206(30)	0.28490(24)	$=B_{iso}$(N1)
	0.02092	**0.63455**	**0.28300**	
H1	−0.07366	0.64595	0.38732	2.821(36)
	0.07536	**0.64340**	**0.38379**	
H2	−0.05493	0.67347	0.17233	$=B_{iso}$(H1)
	0.06191	**0.66450**	**0.16860**	
H3	0.60792	0.14013	0.12374	$=B_{iso}$(H1)
	0.60645	**0.13694**	**0.12196**	
H4	0.58979	0.32474	−0.01599	$=B_{iso}$(H1)
	0.58677	**0.31911**	**0.01674**	

Graph sets can be used to identify hydrogen bonding patterns[5]. The general notation is $G_d^a(n)$, where G is the descriptor and indicates the type of network: S = intramolecular; D = finite, isolated patterns; R = rings; C = infinite chains. The superscript a indicates the number of acceptor atoms and the subscript d gives the number of donor atoms. If $a = d = 1$, they are not included in the graph set symbol. The degree n is the total number of atoms in the pattern, counting *via* the shortest route. It is not defined for patterns of type D. A motif, or unitary graph set is a hydrogen-bonded set in which only one chemically distinct type of hydrogen bond is present. A binary graph set is a descriptor of a pattern in which two types of hydrogen bonds are present.

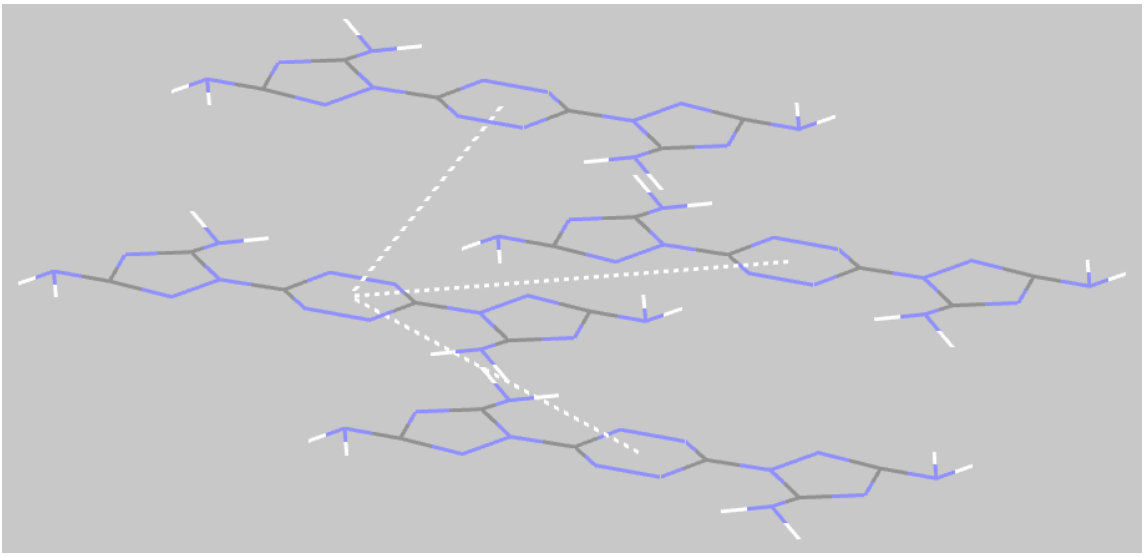


Figure S3. A visualization of molecular aggregate showing mutual orientation of the most strongly interacting species in the crystal.

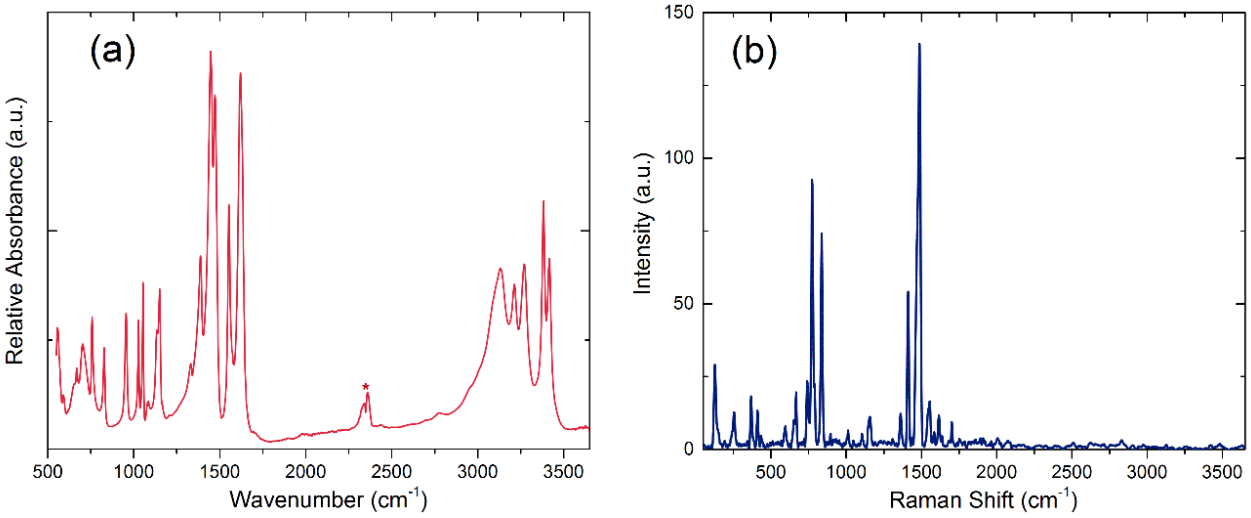


Figure S4. Experimental ATR-FTIR (a) and Raman (b) spectra of IEF-12. Asterisk symbol denotes unsubtracted peak of CO_2 of ambient atmosphere.

Table S4. Calculated vibration mode frequencies and intensities, Mulliken notation symmetry and activity in IR and Raman spectra are denoted for each individual vibration mode.

N vibration	Frequency (cm-1)	Symmetry	IR Intensity (dyn^2 $Å^{-2}$ amu^{-1})	IR activity	Raman activity
1	-0.055007	A_u	0.0000000	No	No
2	-0.045047	A_u	0.0000000	No	No
3	-0.031828	A_u	0.0000000	No	No
4	75.528654	A_g	0.0000000	No	Yes
5	79.045271	A_u	0.0550710	Yes	No
6	107.460585	A_u	0.0806900	Yes	No
7	112.895333	A_g	0.0000000	No	Yes
8	119.597457	A_u	0.1842655	Yes	No
9	121.411207	A_g	0.0000000	No	Yes
10	141.579985	A_g	0.0000000	No	Yes
11	148.446740	A_u	1.7934257	Yes	No
12	155.745938	A_g	0.0000000	No	Yes
13	204.138005	A_g	0.0000000	No	Yes
14	234.153572	A_u	0.6066515	Yes	No
15	241.496778	A_g	0.0000000	No	Yes
16	266.558315	A_g	0.0000000	No	Yes
17	323.420294	A_u	1.2844975	Yes	No
18	328.034051	B	0.0000000	No	Yes
19	351.633768	A_u	2.4780203	Yes	No
20	356.629129	A_u	4.6755734	Yes	No
21	370.554922	A_u	1.5379027	Yes	No
22	372.751023	A_g	0.0000000	No	Yes
23	409.308646	A_g	0.0000000	No	Yes
24	434.826748	A_g	0.0000000	No	Yes
25	491.342546	A_u	5.9728505	Yes	No
26	504.545810	A_u	0.3885084	Yes	No
27	531.768088	A_g	0.0000000	No	Yes
28	534.471132	A_u	18.0908622	Yes	No
29	578.134071	A_u	16.5518131	Yes	No

30	587.883637	A_g	0.0000000	No	Yes
31	602.500506	A_u	0.9108257	Yes	No
32	652.951951	A_g	0.0000000	No	Yes
33	655.029326	A_g	0.0000000	No	Yes
34	665.101978	A_u	0.2380633	Yes	No
35	674.933459	A_g	0.0000000	No	Yes
36	680.097765	A_u	0.2595470	Yes	No
37	722.268852	A_g	0.0000000	No	Yes
38	734.528616	A_g	0.0000000	No	Yes
39	736.413339	A_u	0.6980574	Yes	No
40	757.432617	A_g	0.0000000	No	Yes
41	770.211706	A_g	0.0000000	No	Yes
42	784.567153	A_g	0.0000000	No	Yes
43	788.561630	A_u	6.4258327	Yes	No
44	798.838339	A_g	0.0000000	No	Yes
45	802.395316	A_u	12.4239292	Yes	No
46	837.484314	A_u	5.7283158	Yes	No
47	842.752942	A_g	0.0000000	No	Yes
48	1003.402285	A_u	10.4989742	Yes	No
49	1016.552234	A_g	0.0000000	No	Yes
50	1040.532736	A_u	3.6895462	Yes	No
51	1060.351452	A_g	0.0000000	No	Yes
52	1076.741139	A_u	0.3458482	Yes	No
53	1092.861316	A_u	6.4855663	Yes	No
54	1109.040617	A_g	0.0000000	No	Yes
55	1124.767919	A_u	6.0858801	Yes	No
56	1134.263755	A_u	0.9425430	Yes	No
57	1154.253339	A_g	0.0000000	No	Yes
58	1157.405713	A_u	11.2464934	Yes	No
59	1170.348179	A_g	0.0000000	No	Yes
60	1339.481326	A_u	0.0156785	Yes	No
61	1357.949059	A_g	0.0000000	No	Yes
62	1380.046042	A_u	14.7181448	Yes	No
63	1416.793778	A_g	0.0000000	No	Yes

64	1428.278643	A_u	65.6408282	Yes	No
65	1440.530491	A_g	0.0000000	No	Yes
66	1473.217653	A_g	0.0000000	No	Yes
67	1475.285363	A_u	38.1503195	Yes	No
68	1495.223693	A_g	0.0000000	No	Yes
69	1510.377777	A_u	18.5774410	Yes	No
70	1513.554354	A_g	0.0000000	No	Yes
71	1530.335054	A_g	0.0000000	No	Yes
72	1538.859662	A_u	2.7399769	Yes	No
73	1594.589288	A_g	0.0000000	No	Yes
74	1604.345524	A_u	58.9564865	Yes	No
75	1639.927005	A_g	0.0000000	No	Yes
76	1640.824741	A_u	12.7055803	Yes	No
77	2971.427427	A_g	0.0000000	No	Yes
78	3000.305012	A_u	156.0838273	Yes	No
79	3121.766451	A_g	0.0000000	No	Yes
80	3143.052538	A_u	67.5759421	Yes	No
81	3349.057279	A_u	30.5933281	Yes	No
82	3349.586560	A_g	0.0000000	No	Yes
83	3460.022731	A_g	0.0000000	No	Yes
84	3460.636999	A_u	29.6278511	Yes	No

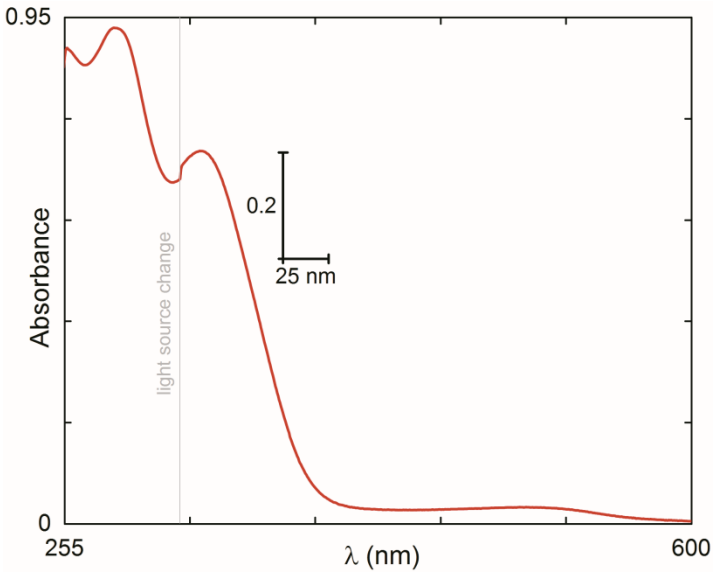


Figure S5. UV-vis absorption spectrum (3.3×10^{-6} M, DMSO) of IEF-12. Grey line stands for a light source alternation and it is shown as a guide for eyes only.

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