Supplementary Information

Packing diagrams of compounds **2** and **3** highlighting some surrogate interactions.

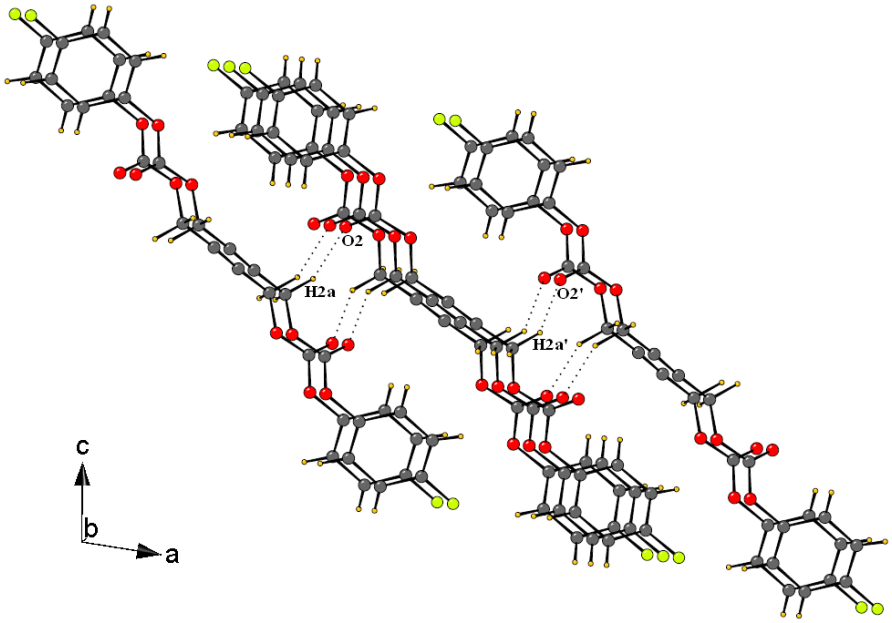


Fig. S1 Packing diagram of **2** showing the cross-linking of molecular chains (shown in fig. 2b) through weak C-H…O [C(2)-H(2a)…O(2), 2.42(1) Å, 131(2)°] interactions involving the carbonyl oxygen.

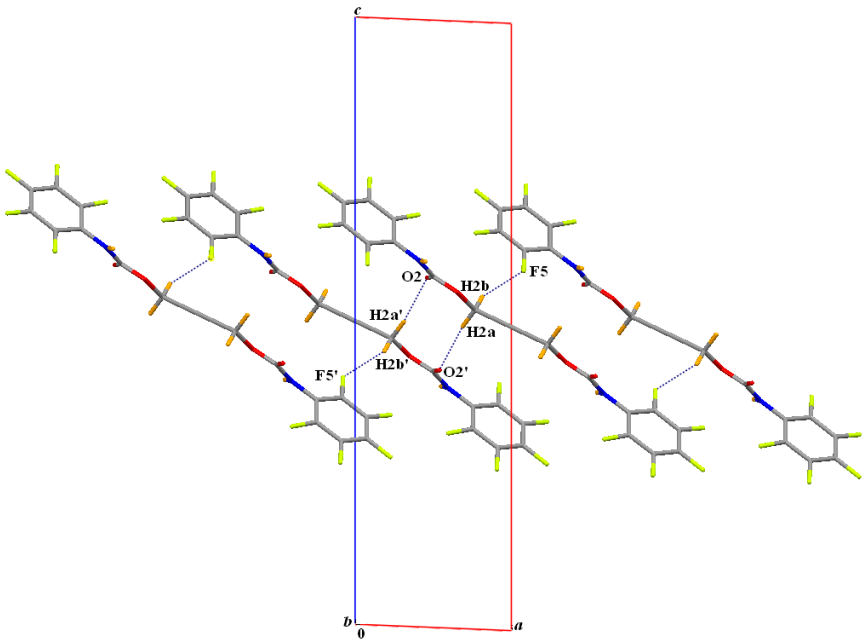


Fig. S2 Packing diagram of **3** showing the cross-linking of molecular chains (shown in fig. 3b) through C-H…O [C(2)-H(2a)…O(2), 2.73(2) Å, 163(2) °] and C-H…F [C(2)-H(2b)…F(5), 2.50(3) Å, 152(2) °] interactions.

Cohesive energy calculations using CRYSTAL09 package[#]

The cohesive energy of a molecular crystal is the energy difference between the total energy of the unit cell and the isolated single molecule in the gas phase. It corresponds to the packing energy due to the interaction among the molecules in the crystal. For comparatively rigid molecules (i.e. those having almost similar geometry in gas phase and in crystal) the cohesive energy expression reduces to:

E(cohesive energy) = ΔE(cond) + BSSE

Where,

ΔE(cond) = E(bulk)/Z - E(mol, bulk);

BSSE = E(mol, bulk) - E(mol, ghosts)

The terms have the following meanings,

E(bulk) = Total energy of the unit cell and must be referred to the value of Z (number of molecules in the unit cell, here Z = 2 for structures 1 (primitive cell), 2 and 3).

E(mol, bulk) = Energy associated with a single molecule having the same geometry as in the bulk.

E (mol, ghosts) = Calculated energy of a single molecule with augmented basis set by using ghost functions on the surrounding atoms.

All calculations were performed at HF/6-31g** level by adopting the experimental structures determined at 90K (compound 1) and 150 K (compounds 2, 3).

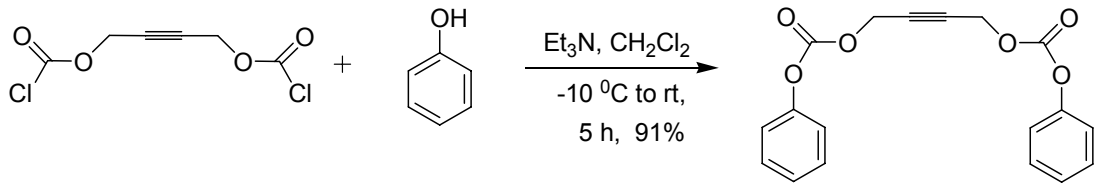
Table S1

	E(bulk) (Hartrees)	**E(mol,bulk) (Hartrees)**	**E(mol,ghost) (Hartrees)**	**ΔE(cond) (kcal/mol)**	**BSSE (kcal/mol)**	**E(cohesive energy)(Kcal/mol)**
1	-4254.605237	-2127.286499	-2127.289381	-10.115188	1.808526	-8.306661
2	-2672.941402	-1336.454502	-1336.458413	-10.164682	2.453966	-7.710716
3	-4174.943727	-2087.449911	-2087.454890	-13.775207	3.124384	-10.650822

[#] R. Dovesi, R. Orlando, B. Civalleri, R. Roetti, V. R. Saunders and C. M. Zicovich-Wilson, Z. Kristallogr., 2005, 220, 571-573.
R. Dovesi, V. R. Saunders, R. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco and M. Llunell, CRYSTAL09, (2009) CRYSTAL09 User's Manual. University of Torino, Torino.

Synthesis and characterization of But-2-yne-1,4-diyl bisphenylcarbonate

But-2-yne-1,4-bisoxycarbonylchloride (**BbcCl**) (0.6g, 2.8 mmol, 1 eq) was added to a stirred solution of phenol (0.53 g, 5.6 mmol, 2 eq) in dichloromethane (20 ml) at -10 °C. The solution was stirred for 10 min and triethylamine (0.86 ml, 6.2 mmol, 2.2 eq) was added drop wise over a period of 10 min. After 5 hrs, the reaction mixture was diluted with dichloromethane (30 ml) and washed with 0.5 N HCl (15 ml), water (2×15 ml) and brine solution (15 ml). The organic layer was dried over anhydrous Na_2SO_4 and the product was purified by column chromatography on silica gel (100-200 mesh), eluting with 5 % solution of ethyl acetate in hexane.



Physical state: Colourless gummy liquid

FTIR (Neat): 3065(m), 2952(m), 1766(s), 1593(m), 1207(s)

^{1}H NMR: δ 7.39-7.21 (m, 5 H), 4.87 (s, 2H)

^{13}C NMR: δ 152.55, 150.53, 129.06, 125.72, 120.47, 80.76, 55.36

High resolution ESMS (m/z): calculated for $C_{18}H_{14}O_6$+Na: 349.0688

Observed: 349.0670