Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for: Predicting the bulk modulus of single-layer covalent organic frameworks with square-lattice topology from molecular building-block properties

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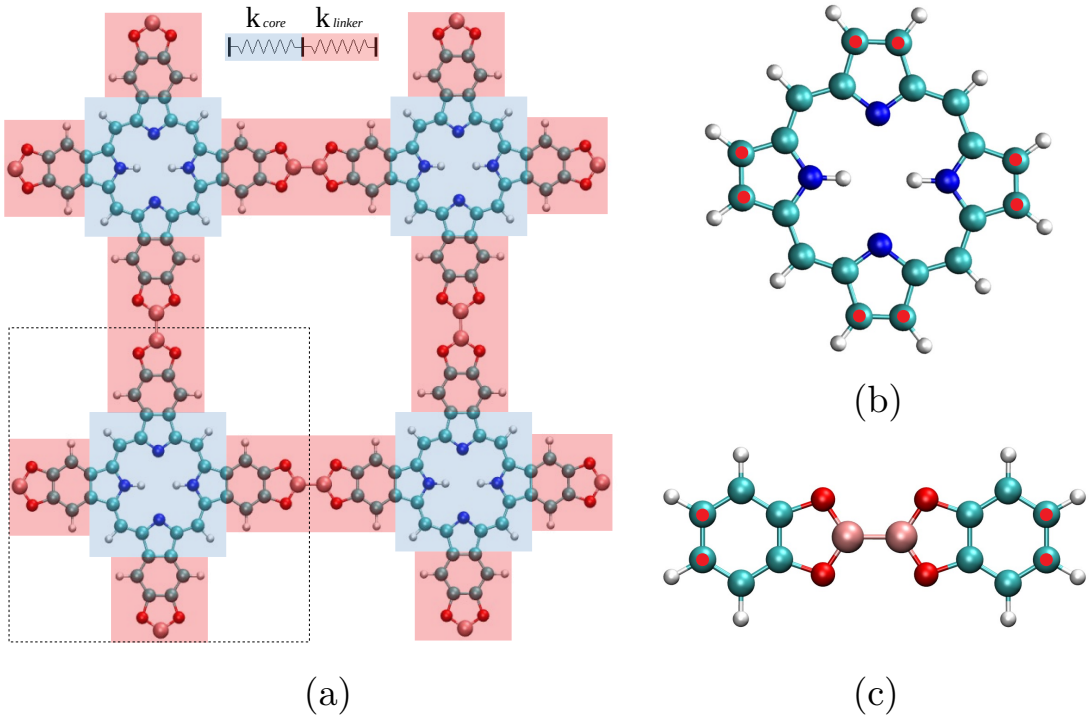


Figure 1: (a) DP-TBPor-COF with the dashed lines indicating the unit cell and the shadowed areas indicate the linker and core molecules. (b) One of the core molecules: porphyrin, and (c) one of the linker molecules: bis(catecholato)diboron. The red circles indicate the applied constraints for the calculation of the equivalent spring constants. Green balls are carbons, light grey balls are hydrogens, blue balls are nitrogens, red balls are oxygens and light brown balls are borons.

Summary of DFTB calculation results for different parametrizations

Table 1: Spring constant calculation with different Slater-Koster parametrizations for specific molecules

Spring constant (N/m)				
Paramterization	**Phenazine**	**Anthracene**	**N-phthalimido phthalimide**	**Porphyrin**
3ob-3-1	224	208.3	112.2	146.8
matsci-0-3	246.8	221.1	147.4	163.8
mio-1-1	229.1	219.5	121.8	163.2
ob2-1-1	264.4	253.1	136.2	176.7
pbc-0-3	229.1	214.7	40.1	160.7
DFT-LDA	219.5	221.1	131.4	132.2
DFT-PBE	224.3	193.9	141.0	134.4

Table 2: Bulk modulus with different Slater-Koster parametrization for specific linker molecules

Bulk modulus (N/m)				
Paramterization	**Azo-TBPor-COF**	**Phenazine-TBPor-COF**	**Anthracene-TBPor-COF**	**PP-TBPor-COF**
3ob-3-1	24.7	48.1	46.9	24.5
matsci-0-3	24.3	51.6	49.2	26.7
mio-1-1	26.6	51.5	50.2	23.2
ob2-1-1	28.5	57.7	56.7	26.7
pbc-0-3	26.5	50.7	49.6	3.8
DFT-LDA	22.4	51.8	45.1	29.7
DFT-PBE	23.7	42.6	43.5	

Equivalent spring constants and bulk moduli

If a molecule consists of n fused fragments with spring constant k, the total equivalent spring constant is given by

$$\frac{1}{k^{(n)}} = \sum^{n} \frac{1}{k} = \frac{n}{k} \, . \tag{1}$$

Assuming anthracene as the reference structure, the equivalent spring constant can be written as

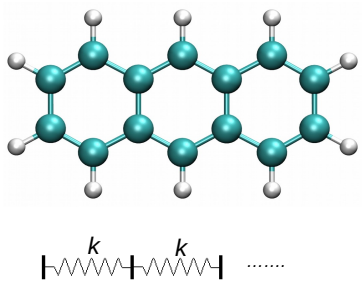
$$k^{(n)} = \frac{3 \cdot k^{(3)}}{n} \, . \tag{2}$$

For example, heptacene has $k^{(7)} = \frac{3}{7} \cdot k^{(3)}$.

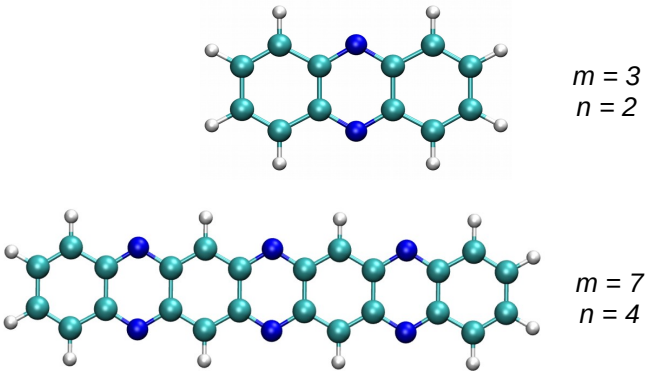
Similarly, *phenazine* (upper part of Fig. 2(b)) has two nitrogens replacing two carbon atoms of anthracene at the internal fused ring. If the total number of rings is three ($m = 3$), but two of them are with carbons ($n = 2$) and considering $m = 2 \cdot n - 1$, the effective spring constant can be written as:

$$\frac{1}{k^{(m)}} = \sum^{m} \frac{1}{k} = \sum^{m} \frac{1}{k_C} + \sum^{m-1} \frac{1}{k_N} = \frac{(k_N + k_C) \cdot m - k_C}{k_N \cdot k_C} \, , \tag{3}$$

where the spring constant of heptacene is denoted by k_C and of 1,4,5,8,9,10-Hexaazaanthracene



(a)



(b)

Figure 2: (a) Anthracene, with the concept that every fused benzene ring can be represented by a spring, so that the molecule contains several springs in series. (b) The upper molecule is phenazine and the lower molecule is diquinoxalino[2,3-b;2',3'-i]phenazine. The total number of rings and the number of rings with substituted carbons by nitrogens are denoted by m and n, respectively.

by k_N. For diquinoxalino[2,3-b;2',3'-i]phenazine (lower part of Fig. 2(b)), where m can be substituted by $(m+1)/2$ and if we consider that $k_C = 3 \cdot k_C^{(3)}$ and $k_N = 3 \cdot k_N^{(3)}$, then equation (3) can be written as

$$k_{C-N}^{(m)} = \frac{6 \cdot k_C^{(3)} \cdot k_N^{(3)}}{(k_C^{(3)} + k_N^{(3)}) \cdot (m+1) - 2 \cdot k_C^{(3)}} \, . \tag{4}$$

If we take *anthracene* and *phenazine* as linker molecules, according to equation (4) of the main text, we can predict the bulk modulus of the corresponding COFs to be

$$B_{COF}^{(n)} = \frac{1}{2} \cdot \frac{k_{\text{core}} \cdot k_{\text{linker}}^{(n)}}{k_{\text{core}} + k_{\text{linker}}^{(n)}} \, , \tag{5}$$

where $k_{\text{linker}} = 3k_n^{(3)}/n$. The spring constant of the core can be eliminated taking the difference between $B_{COF}^{(n)}$ and $B_{COF}^{(3)}$.

$$\frac{1}{B_{COF}^{(3)}} = 2 \cdot (\frac{1}{k_{\text{core}}} + \frac{1}{k^{(3)}}) \, , \frac{1}{B_{COF}^{(n)}} = \qquad \frac{1}{B_{COF}^{(3)}} + \frac{2 \cdot (n-3)}{3 \cdot k^{(3)}} \, . \tag{6}$$

For the case of the fused benzene rings one finds

$$\frac{1}{B^{(n)}} = \frac{1}{B^{(3)}} + \frac{2 \cdot (n-3)}{3 \cdot k^{(3)}} \, . \tag{7}$$

While, for the mixed cases (Fig. 2(b)), a similar approach leads to

$$\frac{1}{B_{C-N}^{(m)}} = \frac{1}{B_{C-N}^{(3)}} + \frac{2 \cdot (m-3)}{3 \cdot k_{C-N}^{(3)}} \, . \tag{8}$$

The equations above can conveniently be used to verify the concept of the effective spring constants and respective bulk moduli. Accordingly, in Fig. 3 we show those two quantities and apply equations (2) and (4) which yield results in good agreement with the calculations (dashed lines).

For the case of anthracene, the plots of the formulas for spring constant and bulk modulus

show that we can almost perfectly predict the values using the results of the base structure (k = 221.1 N/m). For phenazine, the analytical concept was different, where the spring constant of 1,4,5,8,9,10-Hexaazaanthracene is k_N = 256.3 N/m which is used for the k_{C-N}.

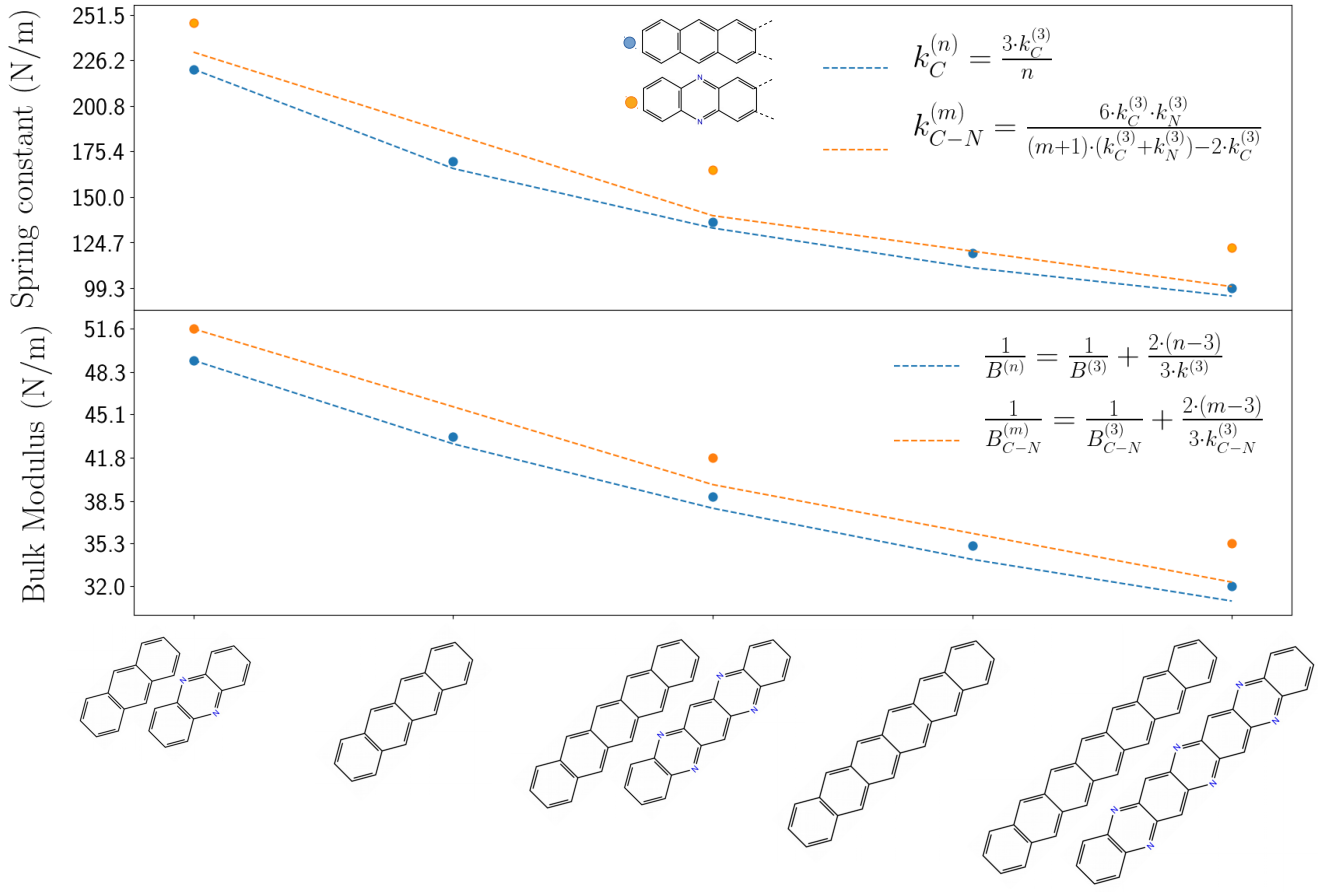


Figure 3: Spring constant and bulk modulus by adding rings to anthracene (from anthracene to heptacene) and phenazine (from phenazine to diquinoxalino[2,3-b;2',3'-i]phenazine). Interrupted lines indicates the fitting according the analytical approach (Equations (2), (4), (7), (8)), while the points show the values of the calculation.

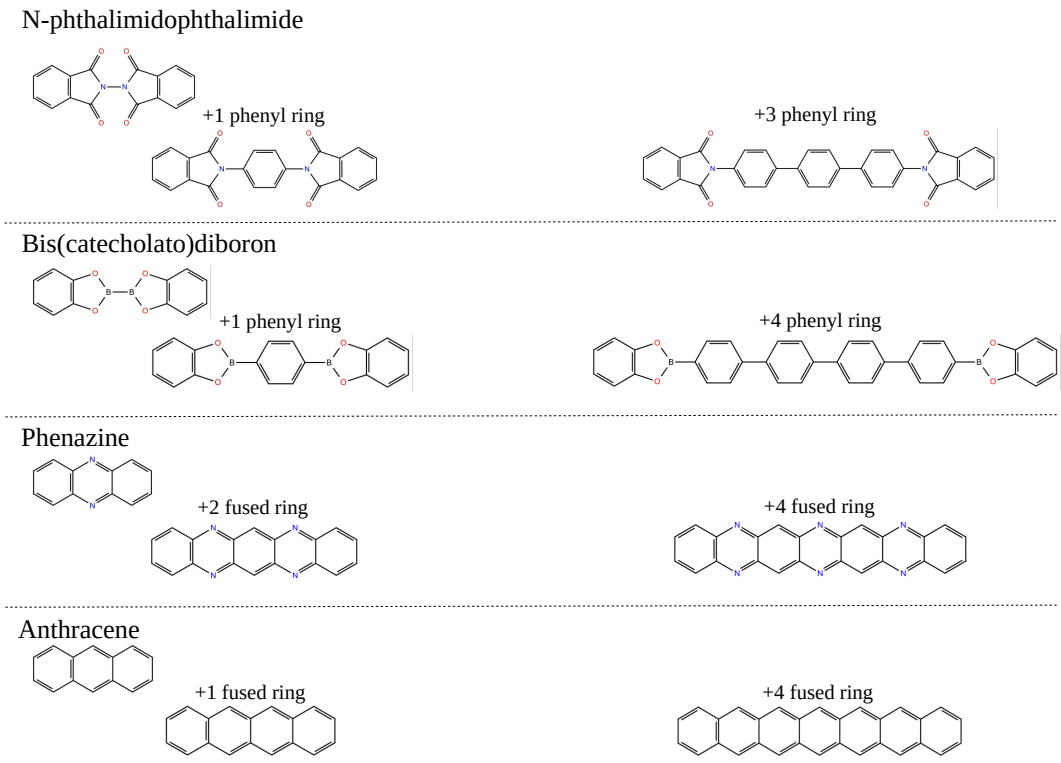


Figure 4: The selected linker molecules for the manipulation of the bulk modulus and the spring constant with examples of added rings to the linker.

Table 3: Results for the spring constants of the linker molecules and the bulk moduli of the COFs with added benzene rings and changing the core (Tetrabenzoporphyrin and Phthalocyanine). In Fig. 4 is the representation of structures with added rings. For the calculation of the COF with four extra rings in the phenazine linker, (15,15,1) k-points were used

Linker	**# rings**	**Spring constant (N/m)**	**Bulk modulus (N/m)**	
			Tetrabenzoporphyrin	Phthalocyanine
N-phthalimidophthalimide	base structure	117	34.1	31.9
	+1	70.5	25.9	24.5
	+2	60.9	21.4	21.6
	+3	49.7	16.7	16.2
bis(catecholato)diboron	base structure	147.4	38.8	37.9
	+1	84.9	29.1	30.7
	+2	62.5	22.8	23.8
	+3	48.1	18.8	19.5
	+4	38.5	16.0	16.4
Phenazine	base structure	246.8	51.6	57.2
	+2	165.0	41.8	45.5
	+4	121.8	35.3	37.8
Anthracene	base structure	221.1	49.2	54.3
	+1	169.8	43.4	47.3
	+2	136.2	38.3	41.9
	+3	118.6	35.1	37.6
	+4	99.3	32.0	34.1