Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

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Constructing (Super)alkali — Boron-Heterofullerene Dyads: An Effective Approach to Achieve Large First Hyperpolarizabilities and High Stabilities in M_3O-BC_{59} (M=Li, Na and K) and K@n-BC_{59} (n=5 and 6)

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The computation on the dipole projection of the first hyperpolarizability (β_μ) and comparison with the total first hyperpolarizability (β_0)

In the main text, only the static first hyperpolarizabilities (β_0) for all the studied systems are provided. Here, we intend to compute the dipole projection of the first hyperpolarizability (β_μ), which is the only tensor component that can be sampled by electric-field-induced-second-harmonic-generation (EFISH) experiment.[1,2] It is expected that the related computations on β_μ can be valuable for further experimental characterization of the studied systems. Note that the β_0 can be identical to β_μ, when the charge transfer is unidirectional and parallel to the molecular dipole moment.[1,3] Of course, it is conceivable that a molecule could have a large nonlinear optical response, but not along the molecular axis sampled by the EFISH measurement, so that β_μ would differ substantially from β_0.

Table S1 lists the computed β_μ values for all the studied systems. It is found that the computed β_μ values can be almost consistent with the corresponding β_0 values. Therefore, for simplicity, only the β_0 was reported in the main text, and the β_μ was included in this Electronic Supplementary Information (ESI).

Table S1. The dipole moment (μ) and its components (μ_i), the vectorial components of the first hyperpolarizability (β_i), the dipole projection of the first hyperpolarizability (β_μ), and the total first hyperpolarizability (β_0) of the studied systems: BC_{59}, K@n-BC_{59} (n=5 and 6) and M_3O-BC_{59} (M=Li, Na and K), respectively. The dipole moment (μ) is in unit of Debye, and the hyperpolarizability (β) is in unit of au.

Systems	BC_{59}	K@6-BC_{59}	K@5-BC_{59}	Li_3O-BC_{59}	Na_3O-BC_{59}	K_3O-BC_{59}
μ_x	-0.46	13.33	-1.85	-1.12	-1.04	-1.14
μ_y	-0.35	-0.38	14.3	14.21	15.70	22.49
μ_z	0	-1.33	0	0	0	0
μ	0.57	13.41	14.42	14.25	15.74	22.52
β_x	999	4127	-3	-191	-555	-809
β_y	258	632	5573	8200	9050	12974
β_z	4	-1287	-396	-6	4	14
β_μ	-579	2527	3316	4914	5438	7799
β_0	619	2621	3352	4921	5440	7800

Note that the XY plane is the symmetry plane in the standard orientation for the species with C_s group.

Subsequently, the specific process for the computation of β_μ is presented as the two following steps:

First, the total dipole moment is defined by

$$\mu = \sqrt{\left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)} \qquad \text{(a)}$$

The unit vector in the direction of the dipole moment is (μ_x/μ, μ_y/μ, μ_z/μ).

Second, a vector component of the first hyperpolarizability along this direction (β_μ) is defined as:

$$\beta_\mu = \frac{3}{5} \times \left(\sum_i \beta_i \mu_i\right) / \mu \qquad i = x, y, z \qquad \text{(b)}$$

Where

$$\begin{aligned} \beta_x &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz}, \\ \beta_y &= \beta_{xxy} + \beta_{yyy} + \beta_{yzz}, \\ \beta_z &= \beta_{xxz} + \beta_{yyz} + \beta_{zzz}, \end{aligned} \qquad \text{(c)}$$

References

[1] D. R. Kanis, M. A. Ratner, and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 10338.
[2] G. Maroulis, *J. Chem. Phys.*, 2000, **113**, 1813.
[3] D. Avci, H. Cömert, and Y. Atalay, *J. Mol. Model.*, 2008, **14**, 161.