

Supporting Information for Molecular Tuning of the Vibrational Thermal Transport Mechanisms in Fullerene Derivative Solutions

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Assumption of Monodispersity

In our analysis, we assume that the fullerene molecules are not influenced by each other and no aggregates are formed. To justify this assumption we perform our thermal measurements at several concentrations (1 mM, 0.2 mM and 0.05 mM). It should be noted that Huxtable *et al.* measured 1 mM solutions of higher order fullerenes in toluene after vigorous centrifugation and found no difference in optical density between the supernatant and the original suspension.¹ Since functionalization generally increases the solubility of fullerenes²⁻⁵ and fullerenes have higher solubilities in 1,2-dichlorobenzene (ODCB),^{2-3, 6} we test the least soluble case, bare C₆₀ in chlorobenzene, which has a solubility, S, of 6.35 mg/mL.²⁻³ We find that the relaxation times are the same for concentrations of 0.05 mM and 0.2 mM but not 1.0 mM, indicating that 0.2 mM solutions are sufficient to avoid aggregation effects. Again, functionalized fullerenes have higher solubilities (*e.g.*, PCBM in chlorobenzene, S = 45 mg/mL),²⁻³ as do fullerenes in ODCB (*e.g.*, C₆₀ in ODCB, S = 22.9 mg/mL).²⁻³ Thus, we are confident that our assumption of monodispersity is justified for all of the solutions examined here.

Time Domain Thermotransmittance Data Analysis

As described in the methods section, we monitor the change in absorption *via* a time domain thermotransmittance (TDTT) approach. Details about these thermometry experiments are described elsewhere.^{1, 7-11} The change in transmissivity of the probe beam at the frequency of the modulated heating event is monitored using a lock-in amplifier. The in-phase signal from the lock-in amplifier is representative of the impulse-response of the sample, *i.e.*, the excitation and relaxation following pump pulse absorption.⁸ Absorption of photons in organic molecules is driven

by conjugated π -electrons.¹² At wavelengths of 400 nm and above, the widely accepted Woodward-Fieser rules¹³⁻¹⁴ exclude the chlorobenzene and *ortho*-dichlorobenzene molecules that compose the liquid and the functional groups on C₆₀ as sources of absorption. Thus, we can assume that the π -electrons within the buckyballs themselves are the absorbing agents in our solutions. Pumped electrons occupy excited states which relax *via* radiative (photon emission) and nonradiative (vibration coupling) processes.¹⁵ Ultrafast pump-probe experiments show electron-vibration coupling occurs on sub-picosecond time scales while excited singlet and triplet lifetimes are on the order of nanoseconds and microseconds, respectively, and are dependent on the functionalization of C₆₀ and the solvent.¹⁵ We are, therefore, confident that the relaxation we observe during our TDDT measurements are indicative of a vibrational relaxation, as shown in previous works.^{1, 16-17}

The biexponential decay function mentioned in the manuscript contains three terms: the first term is used to model the vibrational relaxation, the second to capture electronic effects, and the third is to account for the background (or baseline) absorbance. An example of the raw data (main figure) and model fit (inset) are shown in Fig. S1. The resulting time constants for the vibrational and electronic terms are shown in Fig. S2. Notice that the electronic time constant is dependent on the pump fluence. This is indicative of an electronic process, specifically depletion of the ground state. We do not see this dependence on the vibrational time constant, which provides further evidence that the measured relaxation times are representative of a vibrational process.

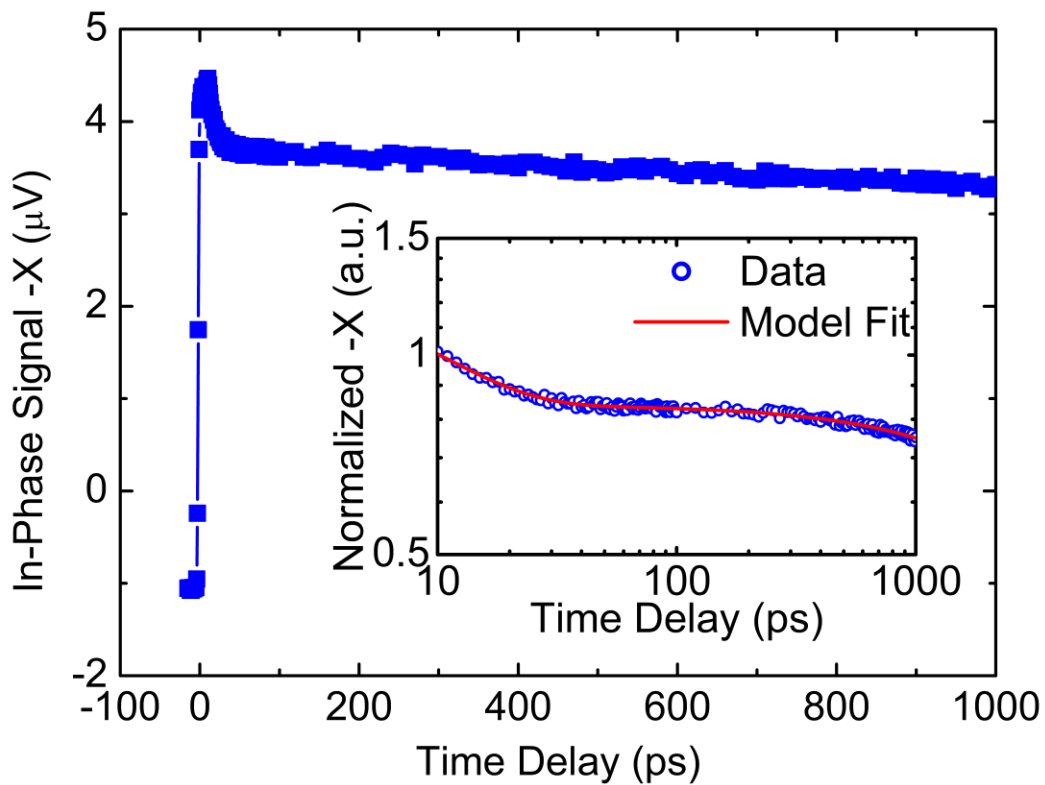


Figure S1. The main figures shows the raw data from a TDDT scan on the PCBM/ODCB solution. After the initial pump excitation we observe biexponential behavior, a fast relaxation followed by a slow one. We normalize the data after the initial peak (~ 10 ps) and fit a biexponential decay curve. The inset shows the normalized data (open circles) with the biexponential model function (solid line). The measured signal continues to relax at a constant rate for the remainder of the TDDT scan (out to 5.5 ns, not shown).

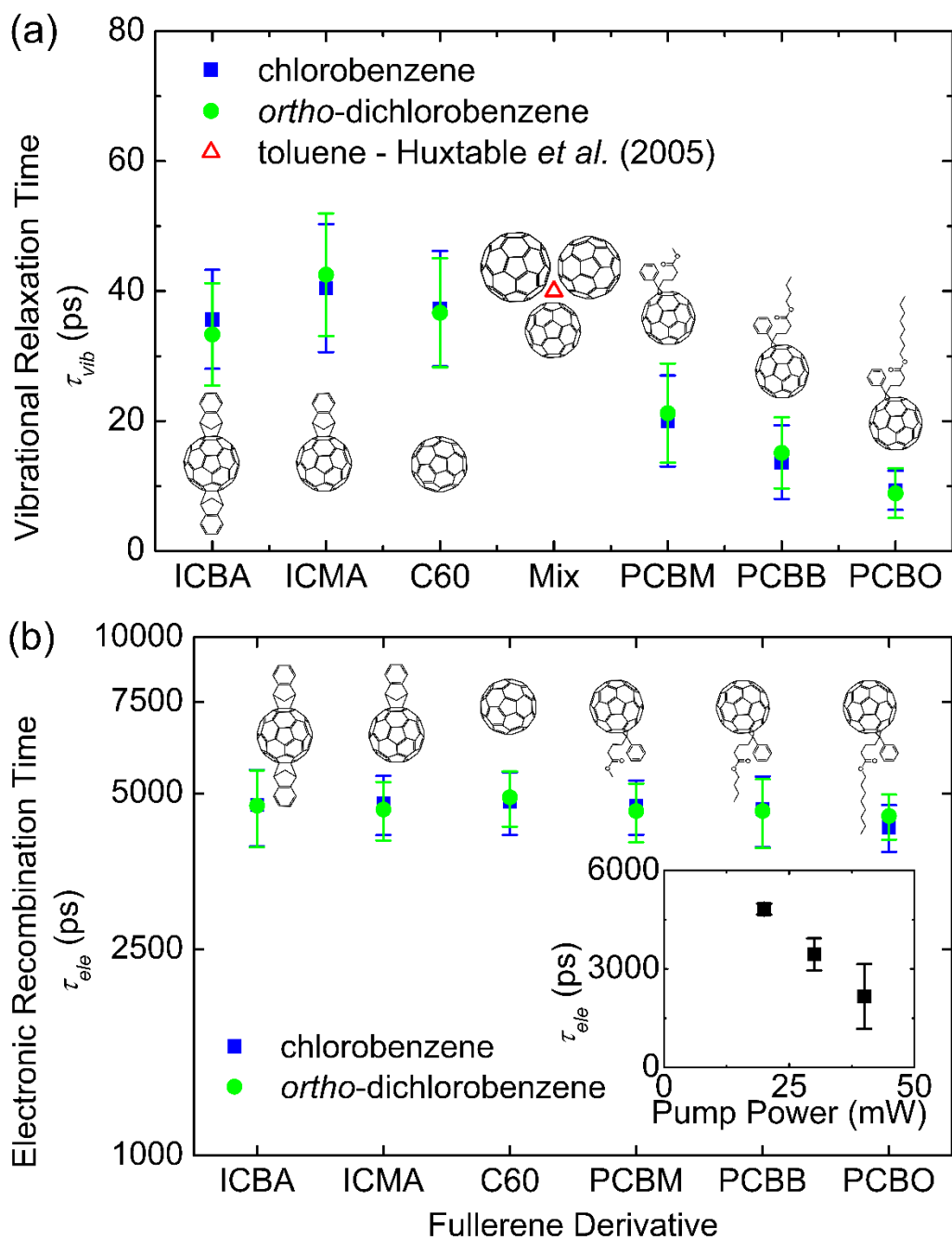


Figure S2. The second time constant corresponds to an electronic recombination time. The inset here shows the measured relaxation time as a function of pump power for which we observe an inverse relationship. We do not observe a dependence on solvent.

Molecular Dynamics Simulations Data Analysis

To gain insight into the effect of functional groups on the relative spectrum of vibrational frequencies of an isolated fullerene molecule or liquid toluene, we implemented classical molecular dynamics simulations using the LAMMPS package.¹⁸ As stated in the manuscript, the velocities of all atoms were recorded every 10 time steps to construct velocity fluctuation time series for a total of 3×10^5 time steps. These time series are then used to obtain the local vibrational density of states (VDOS) for the fullerene molecules or liquid toluene. The details of the process for calculating the VDOS are given in the literature¹⁹ and are reviewed here. The VDOS is proportional to the Fourier transform (\mathcal{F}) of the velocity autocorrelation function (VACF).²⁰ The velocity fluctuation time series is used to build the VACF of which the fast Fourier transform is computed. To compute the VDOS in units of counts per frequency per volume, the following equation is used:¹⁹

$$D(\nu) = \frac{1}{2} m \mathcal{F}(\text{VACF}) \frac{1}{k_B T} \rho,$$

where m is the atomic mass, k_B is the Boltzmann constant, T is the local temperature, and ρ is the atomic density. Plots of the resulting VDOS for the fullerene derivatives considered in this work and liquid toluene are shown in Fig. 3 of the manuscript and again here in Fig. S3.

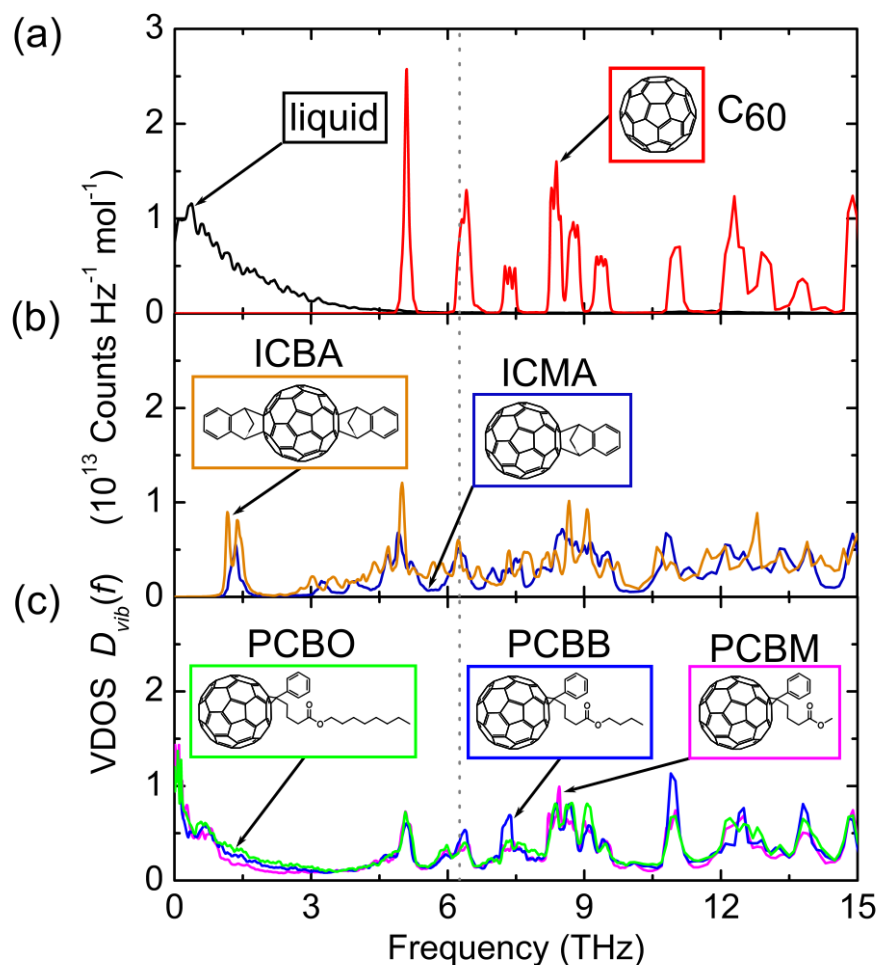


Figure S3. The vibrational density of states at room temperature calculated using MD are shown in panel (a) for liquid toluene (black) and C_{60} (red), in panel (b) for ICMA (navy) and ICBA (orange), and in panel (c) for PCBM (pink), PCBB (blue), and PCBO (green). The gray dotted line denotes the maximum frequency of thermally activated modes at room temperature assuming $\nu_{300\text{K}} = k_{\text{B}}T/h$, below this modes are gradually occupied according to Bose-Einstein distribution.²¹ Simulations of bulk liquid toluene were assumed as a representative benzene-based liquid due to its well ascribed simulation parameters in previous works (see Methods Section).

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