Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for Publication:

Size Onset of Metallic Behavior in Neutral Aluminum Clusters

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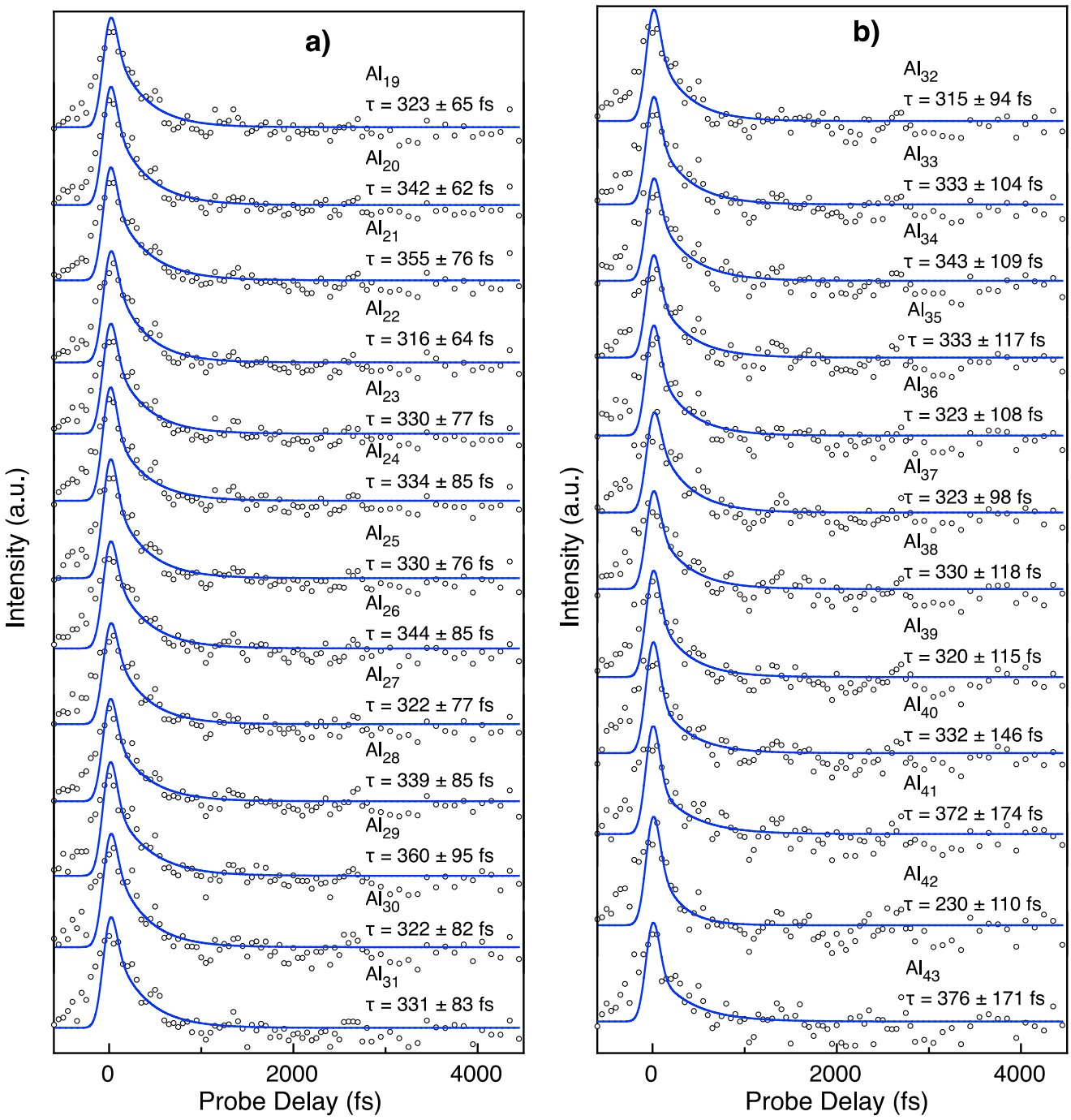

Figure S1. Experimental transient spectra recorded for the larger Al_n clusters where a) $n \in [19, 31]$ and b) $n \in [32, 43]$.

Topological Excited State Calculations

We employ topological descriptors, such as d (distance between the centroids of the electron and hole densities), σ (average root-mean-squared-deviation of the electron and hole), Λ (percent overlap of the electron and hole wavefunctions), and total delocalization index (TDI) to quantify the spatial properties of the charge carrier. The transition densities for the electron and hole were determined as:

$$\rho_e(r) = \sum_{o,v} c_{o,v}^2 \varphi_v^2(r) \quad , \tag{S1}$$

where ρ_e is the electron density at position r, φ represents the spatial wavefunction of a molecular orbital, c_{ov} is the contribution coefficient for each pair, and the subscripts o and v stand for the occupied and virtual pairs involved in the excitation. The hole density, $\rho_h(r)$, is found similarly except using $\varphi_o(r)$. The centroid of the electron density distribution is found following:

$$X_e = \int x\rho_e(r)dr \quad , \tag{S2}$$

where X_e is the centroid position for the x value of the electron. Similar equations are used for y and z coordinates. The distance between the center of the electron and hole, d, is calculated via:

$$d = \sqrt{(d_x)^2 + (d_y)^2 + (d_z)^2} \quad , \tag{S3}$$

where $d_x – |X_e - X_h|$. The σ values are used to characterize their distribution breadths according to:

$$\sigma = \sqrt{\int (r - R)^2 \rho(r) dr} \quad , \tag{S4}$$

where R is the distance from the centroid value for the charge carrier. Large σ values indicate delocalized orbitals. The Λ parameter, which quantifies the degree of overlap between the wavefunctions is found following:

$$\Lambda = \frac{\sum_{o,v} c_{ov}^2 O_{ov}}{\sum_{o,v} C_{ov}^2}, \tag{S5}$$

where the spatial overlap for a given excitation can be obtained by weighting the overlap of each occupied-virtual pair by the coefficient product. Several occupied virtual pairs contribute to a given TD-DFT excitation, and the contribution coefficient of each pair, C_{ov}, is output by Gaussian16. O_{ov} is the spatial overlap between each occupied-virtual pair:

$$O_{ov} = \int |\varphi_o||\varphi_v| dr. \tag{S6}$$

The total delocalization index (TDI) is determined as the average electron and hole delocalization indexes are related to densities as:

$$HDI = 100 \times \sqrt{\int [\rho_h(r)]^2 dr} \tag{S7}$$

$$EDI = 100 \times \sqrt{\int [\rho_e(r)]^2 dr} \tag{S8}$$

Table S1. Transient signal fitting coefficients for Al_n, n = 1-43. $A\tau_1$ and A_{gauss} is the amplitude of the of the exponential decay fit and Gaussian fit, respectively.

Al_n	$A\tau_1$	A_{gauss}	$A\tau_1/A_{gauss}$	Al_n	$A\tau_1$	A_{gauss}	$A\tau_1/A_{gauss}$	Al_n	$A\tau_1$	A_{gauss}	$A\tau_1/A_{gauss}$
2	1.945	2.109	0.922	16	0.451	0.448	1.007	30	0.318	0.204	1.559
3	1.701	0.265	6.419	17	0.582	0.509	1.143	31	0.262	0.179	1.464
4	0.238	0.1	2.380	18	0.467	0.387	1.207	32	0.24	0.212	1.132
5	0.201	0.217	0.926	19	0.54	0.361	1.496	33	0.222	0.201	1.104
6	0.156	0.223	0.700	20	0.565	0.424	1.333	34	0.209	0.176	1.188
7	0.555	0.772	0.719	21	0.478	0.369	1.295	35	0.196	0.184	1.065
8	0.254	0.355	0.715	22	0.569	0.356	1.598	36	0.194	0.183	1.060
9	0.475	0.375	1.267	23	0.497	0.387	1.284	37	0.183	0.125	1.464
10	0.652	0.432	1.509	24	0.445	0.401	1.110	38	0.15	0.138	1.087
11	0.65	0.351	1.852	25	0.432	0.343	1.259	39	0.138	0.14	0.986
12	0.662	0.371	1.784	26	0.358	0.268	1.336	40	0.11	0.138	0.797
13	0.699	0.484	1.444	27	0.38	0.247	1.538	41	0.074	0.112	0.661
14	0.931	0.702	1.326	28	0.328	0.28	1.171	42	0.101	0.095	1.063
15	0.494	0.373	1.324	29	0.263	0.228	1.154	43	0.078	0.104	0.750