The dielectric properties of several supramolecular ionic polymers and networks, linked by the ammonium salts of hexamethylene diamine (HMDA), tris(2-aminoethyl)amine (TAEA), poly(propylene imine) (PPI) dendrimers and two short bis carboxymethyl ether-terminated poly(ethylene glycol)s (DiCOOH-PEG), are reported in this paper. All supramolecular ionic polymers and networks exhibit very high relative dielectric permittivities (3 0) (10 2 – 10 6) at low frequencies, and signifi cantly lower values (from 1 up to 26) at high frequencies. Additionally, the dielectric properties of supramolecular ionic networks, formed by mixing multifunctional carboxylic acids such as citric acid (CA), tricarballylic acid (TCAA), trimesic acid (TMA), ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DETPA) with two different Je ff amine polyetheramines (designated as D400 and D2000), are investigated. Here the relative dielectric permittivities of the supramolecular ionic structures formed with the multifunctional carboxylic acids were lower than those from the supramolecular ionic structures formed with the two carboxymethyl ether-terminated poly(ethylene glycol)s.