

Highly Selective Dispersion of Single-Walled Carbon Nanotubes via Polymer Wrapping: A Combinatorial Study via Modular Conjugation

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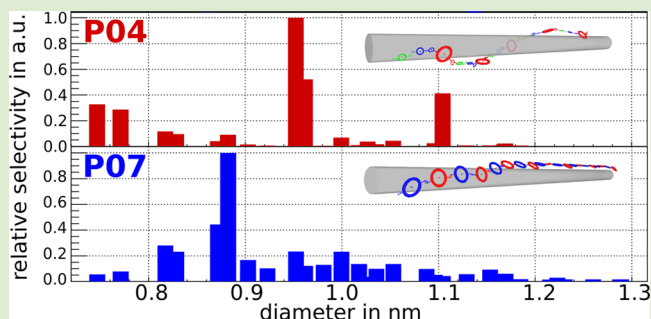
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Supporting Information

ABSTRACT: Fourteen different “hairy-rod” conjugated polymers, 9,9-dioctylfluorene derivatives entailing 1,2,3-triazole, azomethine, ethynyle, biphenyle, and azobenzene lateral units, are synthesized via modular conjugation and are systematically investigated with respect to their ability to selectively disperse SWCNTs. Four polymers of the azomethine type, with unprecedented selectivity toward dispersing (8,7), (7,6), and (9,5) SWCNT species, have been identified. In particular, azomethine polymers, herein applied for the first time for SWCNT dispersion, have been evidenced to be very effective in the highly selective solubilization of SWCNTs. The experimentally observed selectivity results are unambiguously supported by molecular dynamics simulations that account for the geometrical properties and deformation energy landscape of the polymer. Specifically, the calculations accurately and with high precision predict the experimentally observed selectivity for the (7,6) and (9,5) conformations.



The extraordinary physical properties of single walled carbon nanotubes (SWCNT) with applications in the fields of mechanics, optics, and electronics have made this carbon allotrope an outstanding object for scientific research.¹ The chiral index (n,m) and length determine the physical properties of the SWCNTs. Although remarkable progress has been made in the synthesis of chirally uniform SWCNTs,² the current state of the art is still incapable of providing pure monodisperse SWCNTs. Therefore, fractionation methods have to be applied to obtain chirally homogeneous SWCNTs. The methods in use are dielectrophoresis,³ density gradient centrifugation,⁴ size-exclusion chromatography,⁵ and selective dispersion via polymer wrapping.⁶ Nish et al.^{6e} have shown in 2007 for the first time that “hairy-rod” π -conjugated polymers with fluorene units in their backbone are able to selectively dissolve semiconducting SWCNT with large chiral angles. Subsequent to this pioneering work, a significant number of conjugated polymers have been investigated with regard to their ability to selectively disperse SWCNTs and various models to understand selectivity

have been developed.^{6b,7} Variations of the polymer’s aliphatic side chains,⁸ of the aromatic main chain units,⁹ and of the chain length¹⁰ have been explored. Suzuki, Yamamoto, or Kumada coupling are typically used to synthesize the conjugated lateral chain. In the current study, we investigate the SWCNT dispersing properties of a wide range of fluorene polymers within three polymer classes synthesized via modular conjugation in a combinatorial fashion. The aim of the current study is to explore via a systematic investigation the influence of the structural elements in fluorene polymers such as biphenyl, stilbene, and azobenzene. The structural library allowing for such a systematic investigation is based on three distinct chemistries to construct the lateral π -conjugated polymer chain.

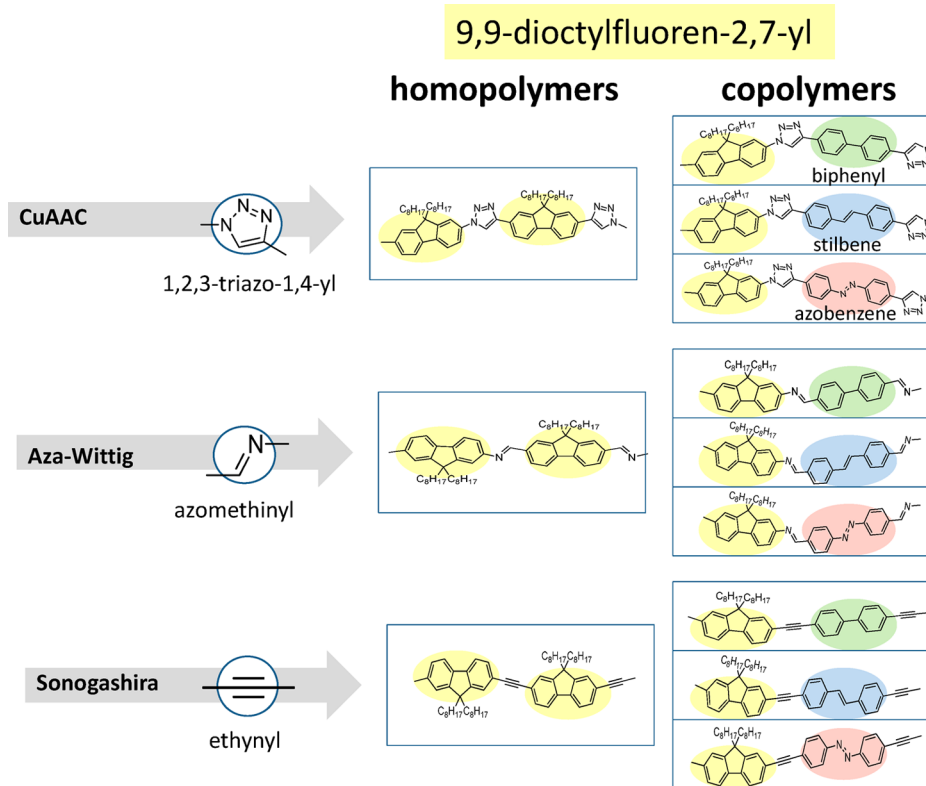
Initially, we employed 1,2,3-triazolyl polymers, generated via copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) of

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Scheme 1. Schematic Overview of the Prepared Polymer Library Employed for SWCNT Dispersion in the Current Study



bifunctional aromatic azides and alkynes. Recently,¹¹ we have shown that these polymers are suitable for SWCNT dispersing. 1,2,3-Triazo-1,4-yl polymers, comprising 9,9-didodecylfluorene units, have shown comparable behavior toward SWCNT as polyoctylfluorene (POF).

Second, we have studied azomethinyl polymers synthesized via aza-Wittig coupling of bifunctional azides and aldehydes. Polyazomethines are π -conjugated polymers with remarkable properties such as electrical conductivity,¹² nonlinear optical features,¹³ the ability to chelate with metals,¹³ and extraordinary thermal stability.¹⁴ Such a polymer type has never been used for SWCNT dispersing. The catalyst-free and uncomplicated synthesis makes aza-Wittig based polymers a highly interesting material platform for SWCNT dispersion.

Third, ethynyl polymers prepared according to the Sonogashira cross coupling reaction from alkynes and bromides have been examined, as Chen et al.¹⁵ have shown that SWCNTs could be dissolved in organic solvents with linear rigid ethynyl polymers.

In each of these three polymer classes, we employed 9,9-dioctyl fluorene as building block incorporated in homo polymers or strictly alternating chains with diphenyl, stilbene or azomethine, resulting in a tableau of 14 different polymers. Scheme 1 depicts the prepared polymer library. Additionally, we synthesized two polymers that exclusively contain fluorene units, yet alternating triazolyl/azoyl or ethynyl/azoyl linkers. Table 1 collates all polymers investigated in the current study jointly with their building blocks.

To classify the performance of the prepared polymer library to selectively dissolve SWCNTs, we introduce four categories. Category 0 includes all polymers which fail to dissolve any SWCNT. Category 1 comprises polymers featuring very weak dispersing power, which are therefore unsuitable for any application. Category 2 contains polymers featuring a good dispersing

capability, yet with no or only a weak manifestation of selectivity. Category 3 represents the polymers with good and highly selective dispersion ability. Table 2 presents a general overview of the PL maps and the solvating category of the polymers. Inspection of the PL-maps of the three polymer classes (refer to Table 2) evidence that the ethynyl polymers are the least suited. Only **P 10** and **P 13** have limited potential, according to category 1, to dissolve SWCNTs. It is expected that the linearly fixed rigid ethynyl connections make the wrapping around the SWCNT extremely difficult and that the solely linear (i.e., parallel to the cylinder axis) association between polymer and SWCNT is too weak for effective dissolution. The investigated triazolyl polymers diverge strongly in their selective properties. Two polymers, **P 02** and **P 03**, fail to dissolve SWCNTs, thus, belonging to category 0. The polymer **P 01** falls into category 1. We recently reported¹⁰ similar fluorenetriazolyl polymers, yet carrying different aliphatic moieties (i.e., dodecyl and hexyl). Caused by their higher solubility in toluene, these systems show better dispersing properties. The polymer **P 05** falls in category 2, with a preference for armchair SWCNTs with $\theta > 20^\circ$ and the (7,6) species as the main dissolved fraction. The polymer **P 04** exhibits strong selectivity toward the (9,5) SWCNTs and falls in category 3. The percentage of the (9,5) SWCNTs observed in solution is close to 47%. Such a result is unexpected, illustrating that small modifications in the lateral polymer chain can cause strong selectivity effects. All azomethinyl polymers **P 06–P 09** fall into category 2 or 3, as they show excellent dispersing properties. **P 09** dissolves several chiral species, especially SWCNTs with $\varnothing > 0.85$ nm. The polymer **P 06** is very highly selective toward the (8,7) species (53%). The polymers **P 07** and **P 08** disperse the (7,6) SWCNT with very high selectivity (46 and 51%). Figure 1 depicts the θ/\varnothing plots of all polymers in categories 2 and 3. The recorded PL intensities

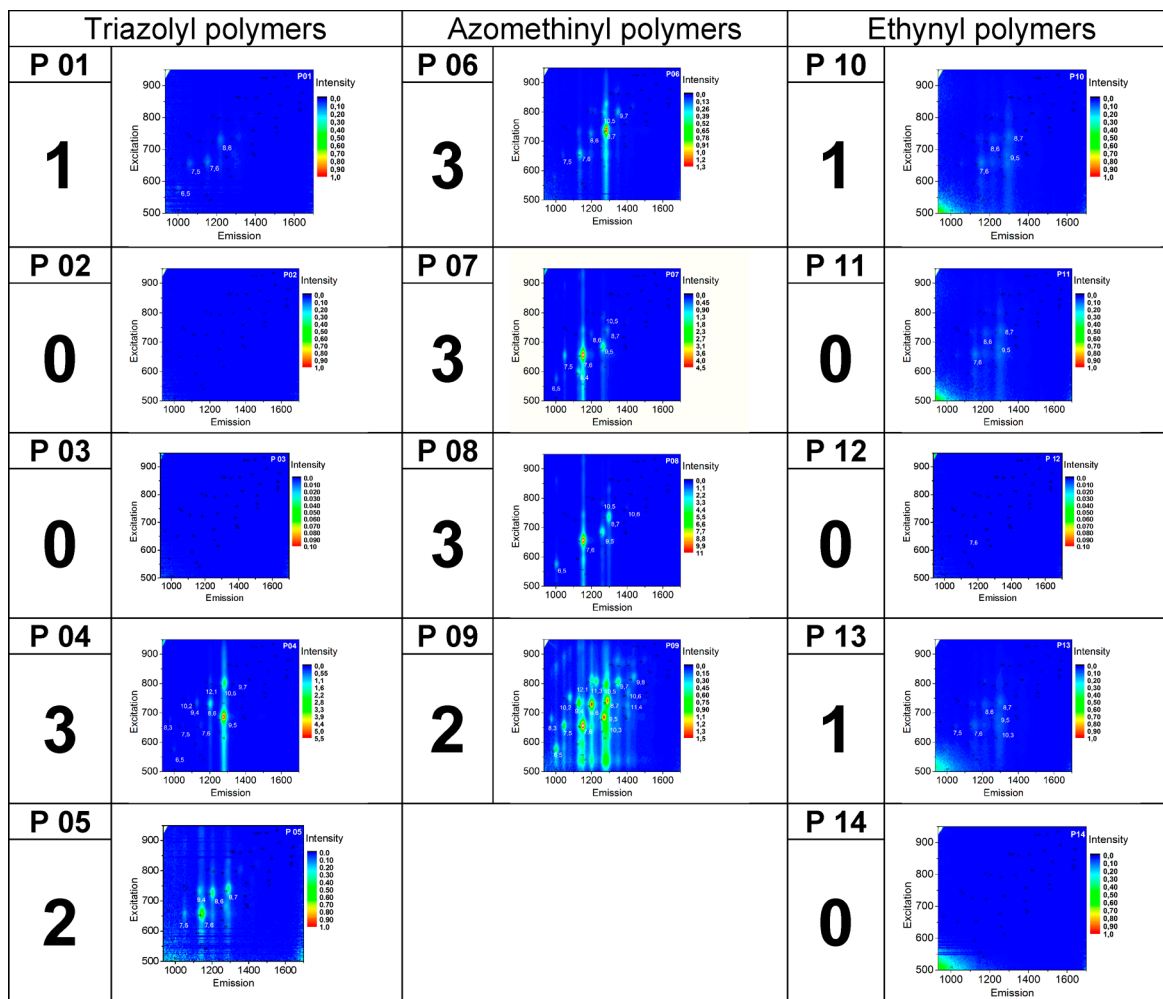
Table 1. Compilation of the Structures and Building Blocks of the Employed Polymers P 01–P 14

Polymer	Structure	Building Blocks	
P 01			
P 02			
P 03			
P 04			
P 05			
P 06			
P 07			
P 08			
P 09			
P 10			
P 11			
P 12			
P 13			
P 14			

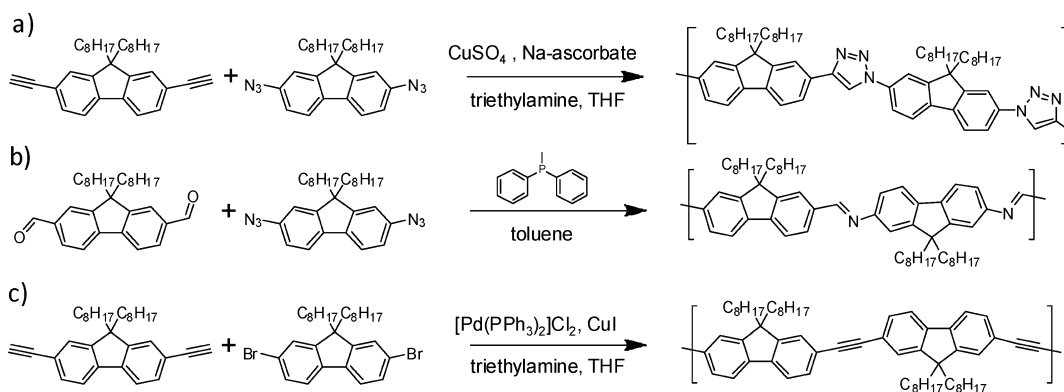
are proportional to the diameters of the black circle, showing the selectivity very clearly.

To rationalize the observed selectivity, we applied the computational protocol outlined below to the most selective polymers, namely, P 04 and P 07. For both polymers and all different diameters, we constructed all mathematically possible solutions of the coarse grained model in which all of the aromatic units of the polymer lie flat on the tube and subsequently weighted them according to the Boltzmann distribution according to their internal energy obtained from a polymer specific ab initio model (for details, refer to the Supporting Information). Figure 2 depicts the weighted number of solutions as a function of

diameter, which clearly demonstrates the diameter selectivity in excellent agreement with the experimental results. As illustrated in the top panel of Figure S3, we note that, in agreement with previous all-atom molecular dynamics simulations for other systems, the number of geometrically possible solutions, in which a given polymer can realize maximal π - π interactions with the tube of a given diameter, is rather small. It is surprising that for some polymers (such as P 10) there are essentially no solutions for any radius (in agreement with the experimental data), while for P 04 and P 07 sets of dihedral angles that permit wrapping of the polymer around a tube for a given radius cease to exist if the radius of the tube is even slightly

Table 2. PLE Maps of the HiPCo SWCNT Suspensions from Polymers P 01–P 14^a

^aA classification number, indicating the dispersing power and the effectiveness of the selectivity is additionally provided: 0 = no dispersion, 1 = weak dispersion, 2 = good dispersion but low selectivity, 3 = good dispersion and high selectivity.

Scheme 2. Synthetic Routes for the Preparation of (a) the 1,2,3-Triazolyl Polymers P 01–P 05; (b) the Azomethinyl Polymers P 06–P 09; and (c) the Ethylnyl Polymers P 10–P 14^a

^aThe fluorine homopolymers are given as example. For the detailed preparation procedures please refer to the Supporting Information.

changed. With hindsight this may be rationalized by the fact that a small dihedral angle change in a macromolecule comprised of relatively rigid building blocks results in a large movement of the units further along the polymer backbone. Apparently such conformational changes induced by one dihedral angle change, which result in a loss of contact between polymer and tube or a

sterically forbidden conformation, cannot be compensated by adjusting the other dihedral angles. This view supports a hypothesis, to be confirmed in future work, that selectivity is obtained as a result of the scarcity of the solutions and suggests exploration of polymers with large rigid building blocks and minimal flexibility to obtain maximal selectivity. In any case, the

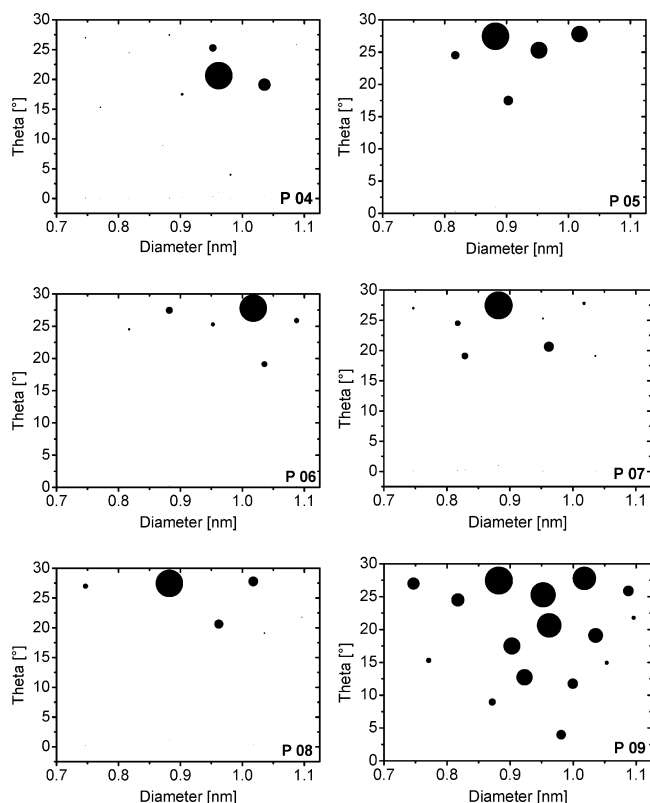


Figure 1. θ/Φ plots of the polymers P 04–P 09. Note the extremely high selectivities of polymer P 04 (9,5), P 06 for (8,7), P 07 for (7,6), and P 08 for (7,6) SWCNTs. Independent, yet virtually identical, θ/Φ plots for polymers P 06 and P 08, based on UV/vis-NIR spectra, are depicted in Figure S4 in the Supporting Information, alongside the underpinning spectral data in Table S2.

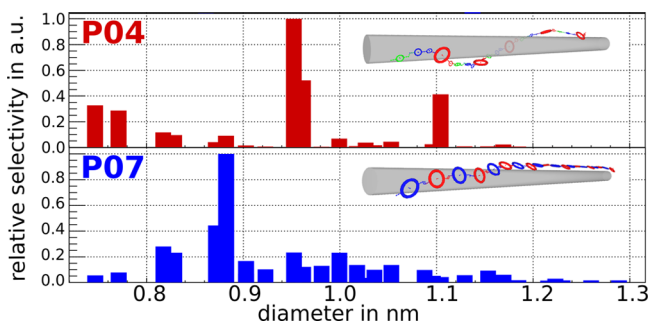


Figure 2. Calculated normalized selectivity of the polymers P 04 (top) and P 07 (bottom) as a function of diameter. Polymer P 04 selectively wraps tubes with 0.96 nm diameter (corresponding to $(n,m) = (9,5)$), while P 07 prefers tubes with diameter 0.88 nm [$(n,m) = (7,6)$].

theoretical predictions show remarkable agreement with the experimental results, which in themselves have identified polymer structures with feature some of the highest selectivity toward specific SWCNT types observed to-date.

In summary, fourteen different “hairy-rod” conjugated polymers, synthesized via modular conjugation, have been systematically investigated with regard to their ability to selectively disperse SWCNTs. All polymers are 9,9-dioctylfluorene derivatives, comprising 1,2,3-triazole, azomethine, ethynyle, biphenyle, stilbene, and azobenzene lateral units. Four polymers have been found to disperse (8,7), (7,6), and (9,5) SWCNT species in a highly selective fashion. In particular, azomethine polymers,

herein applied for the first time for SWCNT dispersion, have been evidenced to be very effective in highly selective solubilization of SWCNTs. Modeling polymer wrapping of the tubes demonstrates that accounting for the geometrical properties and deformation energy landscape of the polymer is essential to understand diameter selectivity. We observed that the existence of polymer conformations in which the polymer wraps around the tube (see inset of Figure 2 for P 04) is responsible for selection of tubes with larger diameters.

METHODS AND MATERIALS

Synthesis of the Polymers: Scheme 2 collates the synthetic pathways for the three polymer classes, giving the 9,9-dioctylfluorene homopolymers as examples. The polymers were synthesized according to slightly modified literature procedures.¹⁶ For the general conditions, the instrumentation, the materials, the synthesis of the building blocks, the polymerization conditions, and the characterization, please refer to the in-depth Supporting Information.

In addition to the fluorene homopolymers [P 01, P 06, P 10], we synthesized strictly alternating copolymers displacing each second fluorene unit with either biphenyl [P 02, P 07, P 11], stilbene [P 03, P 08, P 12], or azobenzene [P 04, P 09, P 13] units, as depicted in Scheme 1 and Table 1. The polymers P 05 and P 14 are special cases. Here, we employed azofluorene as a building block, resulting in polymers with solely fluorene units, yet with alternating linkers [1,2,3-triazolyl-azoyl P 05 and ethynyl-azoyl P 14].

Preparation of the Polymer–SWCNT Dispersions: Dispersions of SWCNTs were obtained by sonicating pristine HiPco SWCNTs (purchased from NanoIntegrals Lot# R0–513 and used as received) in toluene with an excess of the polymer under investigation. Typically, close to 1 mg HiPco SWCNTs were added to a solution of 50 mg of the investigated polymer in toluene (15 mL) and the suspension was sonicated for 1 h. Following an established procedure, centrifugation with a mild centripetal acceleration (10000 rpm, 1 h) was applied to remove large bundles of nanotubes and remaining catalyst particles. The dispersions were analyzed by photoluminescence-excitation spectroscopy (PLE), allowing for the identification and quantification of semiconducting SWCNT species.

Coarse Grained Models for Rationalizing Polymer Selectivity: The computational approach used is described in detail in ref 7b, and in-depth supporting data can be found in the Supporting Information. The polymers were subdivided into molecule specific building blocks, and the intramolecular potentials governing rotation along flexible dihedral angles connecting these blocks were computed using ab initio quantum chemistry methods (for details, please refer to the Supporting Information). A recursive algorithm was used to construct all possible solutions to position a polymer of length $N = 5, 10$ on an SWCNT (for P 04, P 07), respectively (refer to Figure S3 in the Supporting Information), such that all building blocks lie flat on the tube for tubes with diameters ranging from 0.74 to 1.28 nm. The number of solutions for each diameter was weighted with the fraction of tubes with the corresponding diameter in the aqueous sodium cholate SWCNT reference dispersion and with a Boltzmann factor accounting for the intramolecular energy of each solution.

ASSOCIATED CONTENT

Supporting Information

The full synthetic procedures for the polymer systems P 01–P 14, along with their molecular characterization, their building blocks, and UV/vis-NIR spectra, as well as their quantitative evaluation, are provided, as well as in-depth information regarding the molecular dynamics simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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